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Ultraviolet Photoelectron Spectroscopic Studies of Dicarboxylic Acids and Phosphorus Compounds.

Swapan Kumar Chattopadhyay
Louisiana State University and Agricultural & Mechanical College

ULTRAVIOLET PHOTOELECTRON SPECTROSCOPIC STUDIES OF DICARBOXYLIC ACIDS AND PHOSPHORUS COMPOUNDS

A Dissertation

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by
Swapan Kumar Chattopadhyay
B.Sc., Jadavpur University, India, 1970
M.Sc., Jadavpur University, India, 1970
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DEDICATION

To my parents

ACKNOWLEDGEMENTS

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I would also like to thank present and past members of Dr. McGlynn's research group: Dr. P. Hochmann, Dr. J. D. Scott, Dr. W. W. Felps, Dr. G. L. Findley, Dr. K. Wittel, Dr. D. R. Dougherty, Dr. D. Kumar, Mrs. Anne Wahlborg, Miss G. Schoeffler, Mr. D. Bouler, Mr. T. Mathers, Mr. J. Daigneult, Mr. R. Maroun, Mr. V. Shirley, Mr. W. Roland, Miss M. Smith, Miss J. Roberts and Ms. M. Lewis. Thanks are also expressed to Mr. J. Darsey, Dr. J. Lewis, Dr. T. Roberie and Mr. M. Guitrrez. I would also like to thank the rest of the faculty, staff and graduate students at Louisiana State University for their collaboration.

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ABSTRACT

Ultraviolet photoelectron spectra (UPS) of a series of dicarboxyl compounds and a series of phosphorus compounds were obtained.

The investigation of dicarboxyl compounds was undertaken to study the interaction of the carbonyl oxygen lone-pair orbitals. In a dicarboxyl compound, the n MO's, which are designated n_+ and n_-, are split by "through-bond" interaction with the σ MO's which intervene between the carboxyl groups. The spectra of these compounds were interpreted in terms of:

(i) The "through-bond" nature of the interactions involving n-MO's in dicarboxyl compounds.

(ii) The "through-space" nature of the interaction between π_0 MO's of these compounds.

(iii) The effect of O-alkylation on π_0 - MO.

(iv) The "composite-molecule" approach.

The UPS of a series of phosphorus compounds were obtained and the MO assignments made. The changes in the spectral features of phosphites relative to those of the phosphates can be explained in terms of σ-donation and π-acceptance properties of phosphites. Finally, the effects of substitution as well as symmetry lowering can be utilized to rationalize the changes in spectra in going from phosphates to substituted phosphates.

CHAPTER I

INTRODUCTION

In recent years Ultraviolet Photoelectron Spectroscopy (UPS) has evolved into one of the more useful techniques for elucidating molecular electronic structure. The utility invested in the UPS technique is imbedded in the following two considerations:

(i) The UPS experiment is easily performed.[1] However, in terms of precision, UPS data are inferior to those obtainable by the series-limiting technique of Rydberg spectroscopy.[2] Unfortunately, the time-consuming nature of the latter methodology reduces its applicability.

(ii) UPS data are amenable, via Koopmans' Theorem[3], to straightforward theoretical interpretation. According to Koopmans' Theorem, ionization energies, obtained from UPS, are equal (but opposite in sign) to the canonical eigenvalues obtained by a Self-Consistent-Field Molecular Orbital (SCF-MO) processing. To the extent that the theorem is correct (i.e., that the SCF-MO processing is valid), UPS data provide direct measurement of the energies of the filled molecular orbitals of the ground state. Indeed, MO calculations, even if they are of much lower quality than SCF-MO, appear to be a necessary appurtenance to all interpretive UPS efforts.[4]

Unfortunately, since Koopmans' Theorem incorporates two approximations, it may be less general than desired. These approximations are:

- - - - It is assumed that the orbitals of the cationic core are identical to those of the neutral molecule (i.e., no electronic reorganization accompanies electron removal).

- - - - It is assumed that the correlation energy remains unaltered in going from the molecule to the cation.

For valence-shell orbitals, the reorganization and correlation energy

tend to cancel each other.[5] Thus, even though, Koopmans' Theorem may not be theoretically rigorous, its success in the interpretation of UPS data is, to a large extent, attributable to these fortuitous circumstances.[4,5]

This work is concerned with UPS studies of dicarboxylic acids and phosphorus compounds. The purpose of this work is twofold;

(a) To measure and assign the low-energy ionization events in the dicarboxylic acids and to adduce rules concerning the dependance of n-MO splittings on the carboxyl group separations. In view of the importance of the compounds containing dicarboxyl groups in chemistry[6] and biochemistry[7], such a study seems timely.

(b) To measure and assign the low-energy ionization events in phosphorus compounds. Although phosphorus compounds are biologically ubiquitous, little or no discussion of their electronic structure exists.

Since these compounds exhibit diffuse UP spectra and possess little or no fine structure, assignment of these spectra presents some difficulties. Consequently, the useful assignment criteria vested in vibronic structure and perfluoro-effect considerations are inapplicable, and other less-precise methods must be pressed into service. A brief description of these latter assignment criteria seems appropriate at this stage. They are:

A.1 Correlative Studies: UPS data for groups of similar molecules exhibit a certain degree of relatedness. A trend in ionization energies may develop as atoms or groups are inserted into or appended onto the molecule or molecules of interest. These trends, which should also be reproducible in an MO computational mode, can be used

to infer the nature of the various ionization events.

A.2 O-Alkylation Shifts: Those ionization events which remove one electron from a -COOH group are heavily influenced by conversion of the acid into the ester.

A.3 Monoesterification: The ionization events which are associated with removal of an electron from the π_0 MO, (i.e., the MO which is largely localized on the substituent at the carbonyl center) are formally degenerate in those dicarboxylic acids in which the acid groups are separated by at least one carbon atom. However, monoesterification selectively affects one of the carboxyl groups and eliminates this degeneracy.

A.4 "Through Bond" Interactions: The interaction which lifts the degeneracy of the two formally-degenerate n orbitals, which are largely of 2p-type and localized on the oxygen center, via their coupling through the skeletal σ-framework is categorized as "through-bond" interaction.[8] This interaction is the primary cause of the observed splitting of the n-MO's in the dicarboxylic acids. Fortunately, certain empirical rules concerning this splitting are available.[9]

A.5 The Composite Molecule Approach: A composite molecule approach based on the availability of good UPS assignments for the monocarboxylic acids can be used to substantiate the assignments made on the basis of criteria A.1-4 for the dicarboxylic acids.

A.6 Quantum Chemical Calculations: Semi-empirical computational schemes (such as are provided by the CNDO/2[10] and CNDO/s[11] algorithms) can be used in an attempt to provide a counterpart for the individual experimental spectra.

Chapter 2 is concerned with UPS studies of dicarboxylic acids.

Chapter 3 deals with UPS studies of phosphorus compounds.

CHAPTER II

ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY OF DICARBOXYLIC ACIDS

INTRODUCTION

Dicarboxylic acids are abundant in nature, both as ligands and as anions in the Krebs cycle. Since they are readily volatile, they are clearly amenable to UPS studies. Since they are biologically important, it is odd that so little UPS work has been invested in them. This is all the more surprizing because UPS investigations of other monocarbonyls and dicarbonyls are rather plentiful.[12-18]

The two highest-energy occupied MO's (HOMO's) of simple dicarbonyls are the n MO's, which are linear combinations[12,12,24] of oxygen non-bonding 2p atomic orbitals n_1 and n_2. For symmetrical dicarbonyls, these two HOMO's can be described by the symmetry-adapted, semi-localized[12,13] functions:

$$n_+ = \frac{1}{\sqrt{2}} (n_1 + n_2)$$

$$n_+ = \frac{1}{\sqrt{2}} (n_1 - n_2)$$

where the subscripts +/- refer to phasing.

In the zeroth-order approximation, these functions are degenerate. For non-symmetrical dicarbonyl compounds, the corresponding set of functions is non-degenerate even in the zeroth order.

The purpose of this work follows:

(i) To elicit the nature of the interactions which remove the n_+/n_- zeroth-order degeneracy.

(ii) To elicit the dependence of the n-MO splitting on the separation of the carboxyl groups.

(iii) To determine the energetic order of the n_+ and n_- MO's which result from the splitting.

(iv) To assign the π_0 ionization events associated with the carboxyl groups.

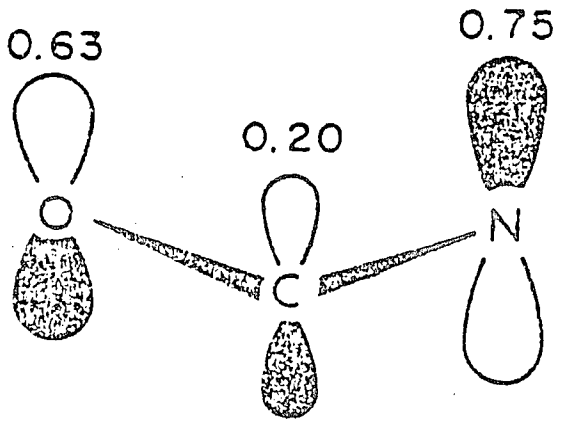
The interactions of item (i), have been explained satisfactorily in terms of the heuristic concept of "through-bond" interaction.[14] Consequently, our efforts will focus, almost exclusively, on items (ii), (iii) and (iv).

The magnitude of the interaction, defined as $\Delta I(n) = |I(n_+) - I(n_-)|$, decreases progressively as the separation between the carboxyl groups increases.[29] $\Delta I(n)$ is ~2, ~0.5, ~0.3, ~0.0 and ~0.0eV for α-, β-, γ-, δ- and ε-dicarboxylic acids, respectively.

Empirical rules which relate the energetic order of the $I(n_+)$ and $I(n_-)$ events to molecular structure have been detailed.[29] Since molecular orbital computations for the dicarboxylic acids support the validity of these same rules for the dicarboxylic acids, we will make extensive use of them.

The π_0 MO's of a dicarboxylic acid are also degenerate in zeroth-order. Before we discuss the interactions of the π_0 MO's a description of them appears to be in order. The π_0 MO is akin to the "ℓ MO" in molecules like aniline or phenol. The π_0 MO computed for formamide[30] is shown in Figure 1. In α-dicarboxylic acids, the formally-degenerate π_0 MO's on each carboxyl group interact by "through space" means to produce $\pi_\ominus$ and π_θ MO's which are no longer degenerate.[31] But as the distance of separation between the carboxyl groups increases, the magnitude of the "through-space" interaction between the π_0 MO's decreases, resulting in the narrowing of the energy gap between the $\pi_\ominus$ and π_θ MO's. Consequently, $\pi_\ominus$ and π_θ ionization events in β-, γ-, δ, and ε- dicarboxylic acids are effectively degenerate. The $\pi_\ominus$ and π_θ MO notation for symmetrical disubstituted dicarboxylic acids is enumerated in Table 1. This notation, while inexact for unsymmetrical dicarboxyl compounds such

Figure 1: Molecular orbital of π_0-type for formamide, as generated in a CNDO/s calculation.[30] Numbers above the π lobes refer to MO coefficients at the center in question.

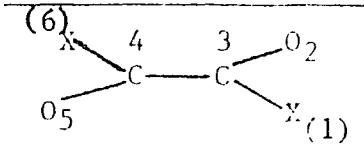
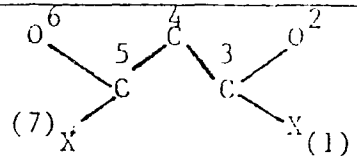
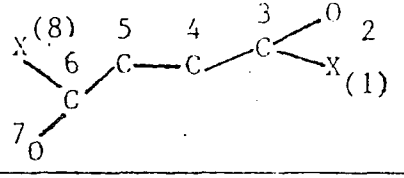
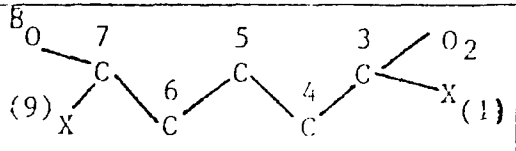
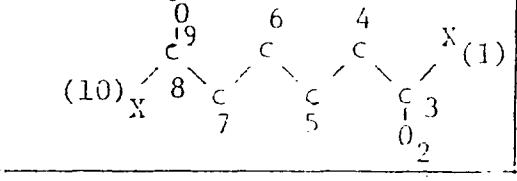


-11.23 eV; $2a''$ (C_s); π_O

as succinamic acid, will be used because of the lack of a better.

TABLE I

π_{ϕ} and π_{θ} MO's of DICARBOXYLIC ACID[a]

Compound Type	Numbering System	π_{ϕ} MO Description	π_{θ} MO Description
Symmetric Disubstituted α-Dicarboxylic Acid		MO (1)2345(6) (-)++++(-)	MO (1)2345(6) (-)++--(+)
Symmetric Disubstituted β-Dicarboxylic Acid		MO (1)23456(7) (-)++-++(-)	MO (1)23 4 56(7) (-)++(•)--(+)
Symmetric Disubstituted γ-Dicarboyxlic Acid		MO(1)234567(8) (-)++--++(-)	MO(1)234567(8) (-)++-+--(+)
Symmetric Disubstituted ε-Dicarboxylic Acid		MO(1)2345678(9) (-)++-+-++(-)	MO (1)234 5 568(9) (-)++-(•)+--(+)
Symmetric Disubstituted ∈-Dicarboxylic Acid		MO (1)23456789(10) (-)++-++-++(-)	MO (1)234 5 6 789(10) (-)++-(•)(•)+--(+)

[a]This Table, constructed after D. B. Larson,[32] has been modified considerably. Hydrogen atoms are not included for convenience. The + and - signs refer to phasing of the wavefunction on the various atomic centers. The use of a bracketed dot indicates zero or near-zero amplitudes on the center in question.

I. EXPERIMENTAL

The He I photoelectron spectra were recorded with a Perkin-Elmer PS-18 cylindrical electrostatic-field deflection analyzer with 10-cm radius. The compounds were ionized with 584Å (21.22eV) He I radiation. The ejected electrons were detected by a Bendix "channeltron" electron multiplier. Solid samples were sublimed in a heated probe, the temperature of which was maintained constant to within $\pm 2^{o}C$ during each spectral run. The $3p_{1/2}$ and $2p_{3/2}$ lines of Xe and Ar were used to calibrate the spectra. The resolution prior to each run was 20-25meV.

All solid samples were purified by vacuum sublimation. Ethyl malonate was prepared according to the procedures of Fourneau.[33]

Quantum mechanical calculations were performed in the QCPE 141-CNDO/2[34] and QCPE 174 - CNDO/s[30] alogrithmic modes.

II. THE INTERACTION MODEL

The individual lone pair AO's on the carbonyl oxygens, n_1 and n_2 are combined in linear fashion to yield n_+/n_- MO's which are semi-localized and degenerate in the zeroth-order. Since the "through-space" interaction between n_1 and n_2 is insignificantly small,[12,15] the removal of degeneracy is almost totally mediated by "through-bond" interactions. The n_+/n_- MO's interact with each other through the connecting skeletal σj orbitals. The characteristics of such a model are:

(i) The interacting n_+/n_- MO's and σj orbitals must transform identically under the operations of the molecular point-group.

(ii) The magnitude of the n_+/n_- and σ_j interactions should vary inversely as the zeroth-order energy separation of the n_+/n_- and σ_j MO's. Consequently, the virtual orbital set, which is of high energy because of its antibonding nature, will not play any significant role.

(iii) The magnitude of the overlaps $\langle n_+ \sigma_j \rangle$ and $\langle n_- \sigma_k \rangle$ determines the interaction matrix elements. Hence, the interaction is dependent to a large extent on the amplitude of σ_j in the proximity of the carbonyl groups.

A. <u>α-Dicarboxyl Compounds.</u> α-Dicarboxylic acids and related compounds have been studied rather extensively.[31] Thus, we shall limit ourselves to a short summary of their characteristics.

(i) The magnitude of "through-bond" interaction is largest in α-dicarboxylic acids and related compounds. Furthermore, the magnitude of interaction is not particularly sensitive to the dihedral angles between the carboxyl units. An interaction scheme which typifies a cis-α-dicarbonyl compound is shown in Figure 2. The same scheme is equally valid for <u>trans</u>-dicarboxyl compounds. From symmetry considerations, only the n_+ MO can mix with the σ skeletal orbital. Hence, the predicted order is $(n_+^{\sigma}) > (n_-^{o})$. (The superscripts "σ" and "o" indicate "mixing" and "no mixing", respectively, with the σ skeletal orbitals.)

(ii) The CNDO/s MO diagram for oxalic acid (<u>trans</u>) is presented in Figure 3. The experimental value of the n_+^{σ}/n_-^{o} splitting is typically ~1.9eV, as is demonstrated in Table 2.

(iii) The formally-degenerate π_0 MO's split. The splitting of π_0 MO's

Figure 2. Schematic diagram of through-bond orbital interactions in α-dicarbonyls. cis-Carbonyl units are shown, but the results are general for any dihedral angle.

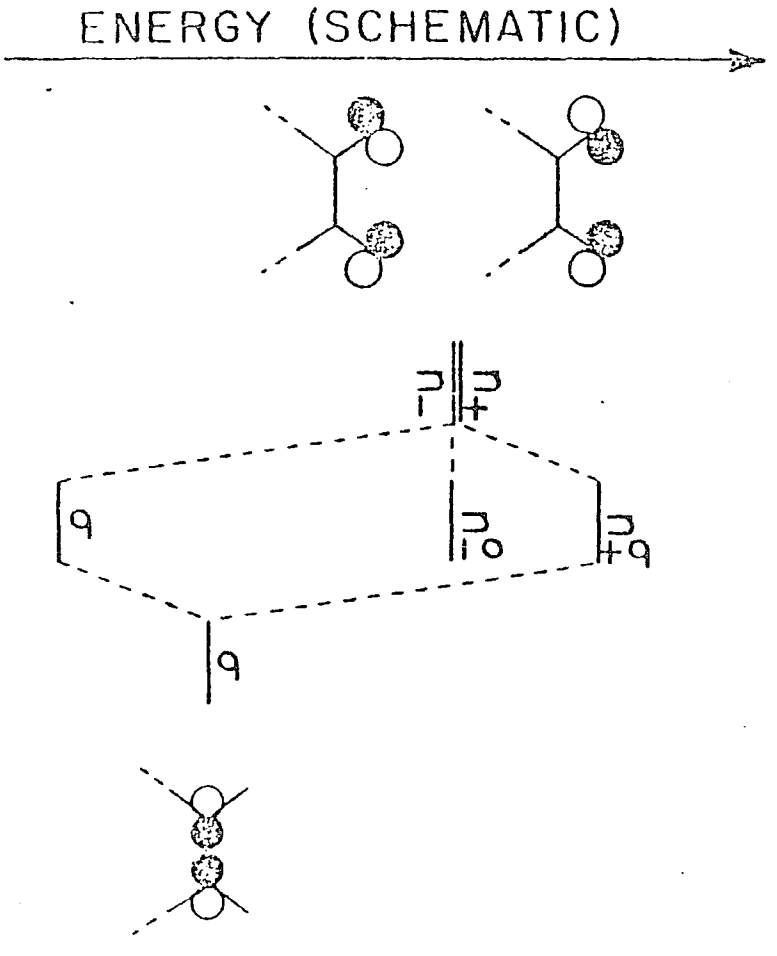
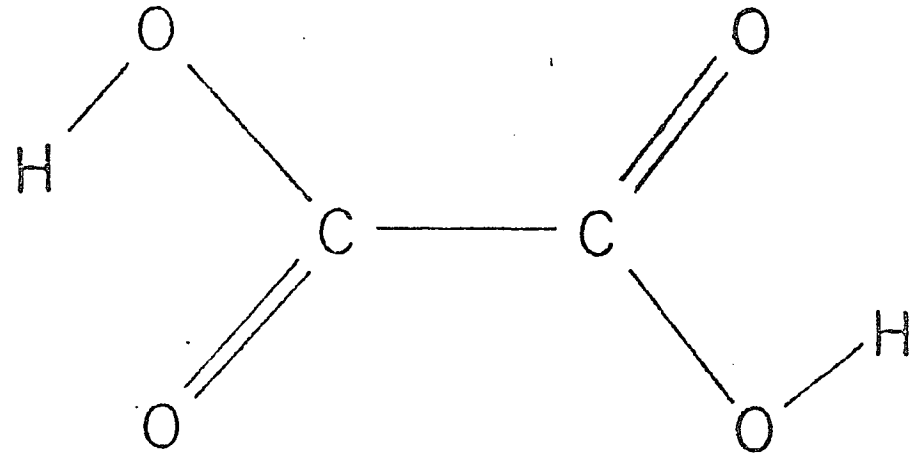
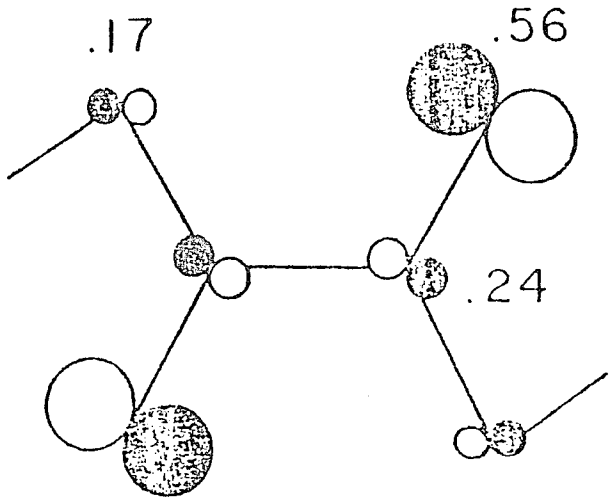
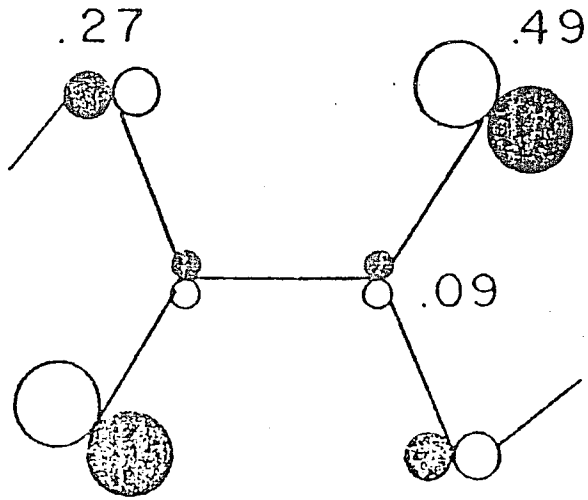

ENERGY (SCHEMATIC)
π−
π+
q
π0
π+q
q

Figure 3. Schematic representation of the n MO's of oxalic acid. LCAO MO coefficients are also shown. The CNDO/s computations were performed at the equilibrium X-ray diffraction geometry.[35]





n_{+}^{σ}



n_{-}^{o}

TABLE 2

VERTICAL IONIZATION ENERGIES (eV) FOR THE

NON-BONDING MO's OF α-DICARBOXYL COMPOUNDS

(The difference Δn is defined as $\Delta n = -I(n_+^{\sigma}) - I(n_-^{o})$)

Number Index	Compound	$I(n_+^{\sigma})$	$I(n_-^{o})$	Δn
1.	HOOCCOOH[a]	11.20	13.25	2.05
2.	$CH_3OOCCOOCH_3$[a]	10.30	11.74	1.44
3.	$C_2H_5OOCCOOC_2H_5$[a]	10.19	11.41	1.22
4.	$NH_2(O)CCOOH$[a]	10.51	12.40	1.89
5.	$C_2H_5OOCCONH_2$[b]	9.85	11.73	1.88
6.	$C_2H_5OOCCON(CH_3)_2$[b]	9.31	11.09	1.78
7.	$C_2H_5OOCCOCl$[b]	10.77	12.76	1.99
8.	$(CH_3)NH(O)CC(O)NH(CH_3)$[c]	9.33	11.20	~1.87
9.	$(CH_3)N(O)CC(O)N(CH_3)_2$[c]	~9.0	10.99	~1.99

a. J. L. Meeks, J. F. Arnett, D. B. Larson and S. P. McGlynn, J. Amer. Chem. Soc., 97, 3905 (1975).

b. J. L. Meeks and S. P. McGlynn, Spectroscop. Letters, 8, 439 (1975).

c. J. L. Meeks and S. P. McGlynn, J. Amer. Chem. Soc., 97, 5079 (1975).

into $\pi_{\oplus}$ and $\pi_{\ominus}$ MO's occurs via "through space" interaction.[31] The splitting of the $\pi_{\oplus}/\pi_{\ominus}$ MO's is ~1.5eV.

B. β-Dicarboxyl Compounds. Malonic acid and dimethylmalonic acid decompose in the solid probe at the T~50°C and their spectra cannot be recorded. Studies of these two compounds involving gaseous probe sampling were equally unsuccessful.

The UPS of ethyl malonate (EM), dimethyl malonate (DMM), diethyl malonate (DEM), diethyl ethylmalonate (DEEM) and diethyl diethylmalonate (DEDEM) are displayed in Figure 4. C_{2v} geometry has been assumed for DMM, DEM and DEDEM. EM and DEEM have C_s geometry. Ionization events and their assignments are tabulated in Table 3. The ionization bands of these compounds are poorly resolved.

Interaction scheme: The "through-bond" interactions in the β-dicarboxylic acid derivatives must propagate through two intervening skeletal σ bonds. Empirical studies of the β-dicarbonyls have established that, for compounds containing non-coasial carbonyl groups, the energetic order of the n MO's is $n_-^{\sigma} > n_+^{o}$, and the splitting is ~0.5eV (which is considerably less than that for α-dicarbonyl compounds). The n MO's are presented pictorially in Figure 5. The conformation shown in Figure 5 corresponds to the equilibrium geometry. An examination of the LCAO MO coefficients indicates that differential mixing with the skeletal σ structure is the factor responsible for the splitting of n MO's. The calculated and observed splittings are tabulated in Table 4. The observed splitting is ~0.5eV. However, the calculated splitting is approximately twice that which is observed. The magnitudes of the observed splitting, however, agrees well with the empirical observations for other β-dicarbonyl compounds.[18] A graph of the calculated and

Figure 4. UPS of EM, DMM, DEM, DEEM and DEDEM.

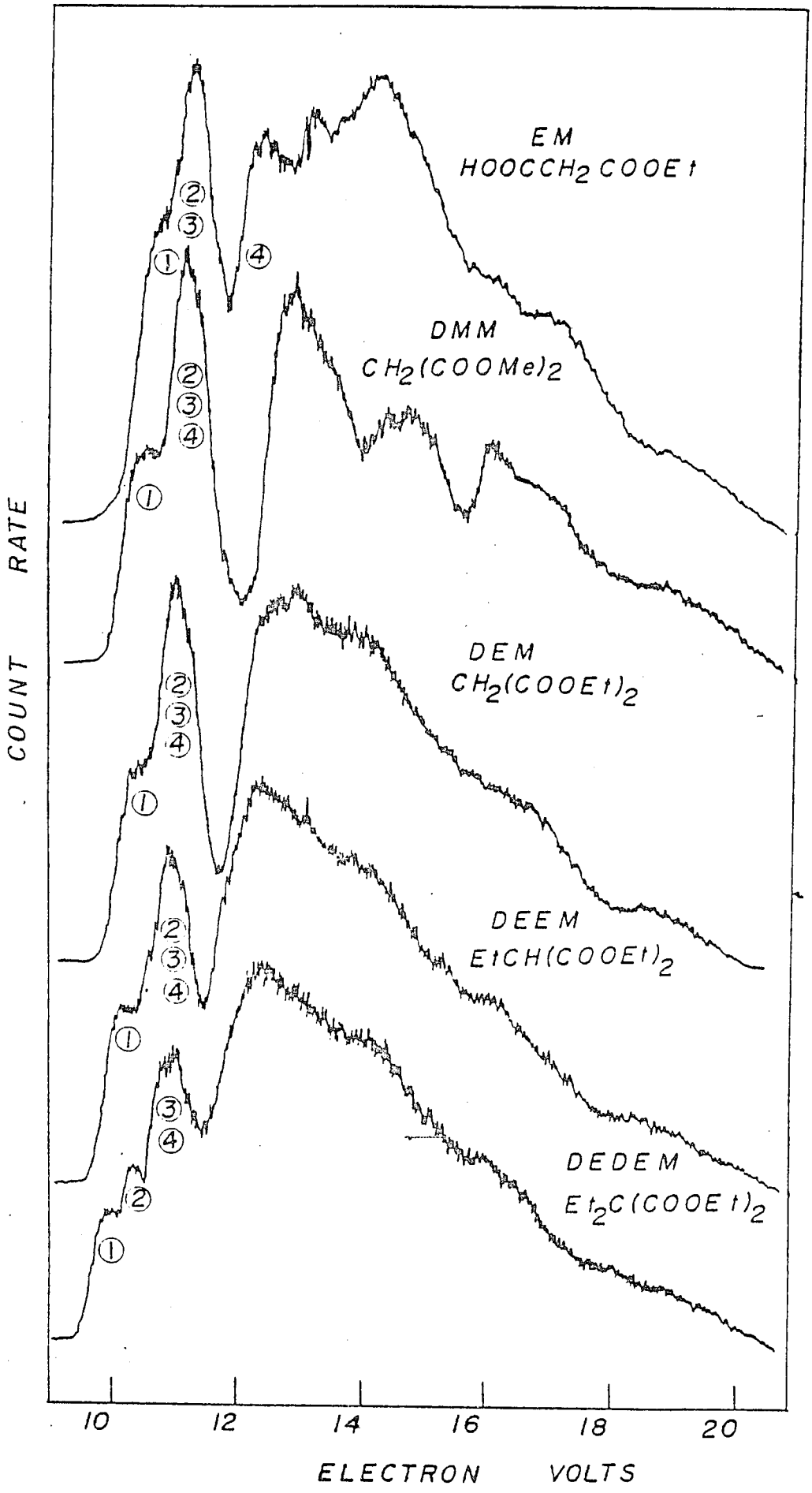

EM
HOOCCH2 COOEt
DMM
CH2(COOMe)2
DEM
CH2(COOEt)2
DEEM
EtCH(COOEt)2
DEDEM
Et2C(COOEt)2
COUNT RATE
10
12
14
16
18
20
ELECTRON VOLTS

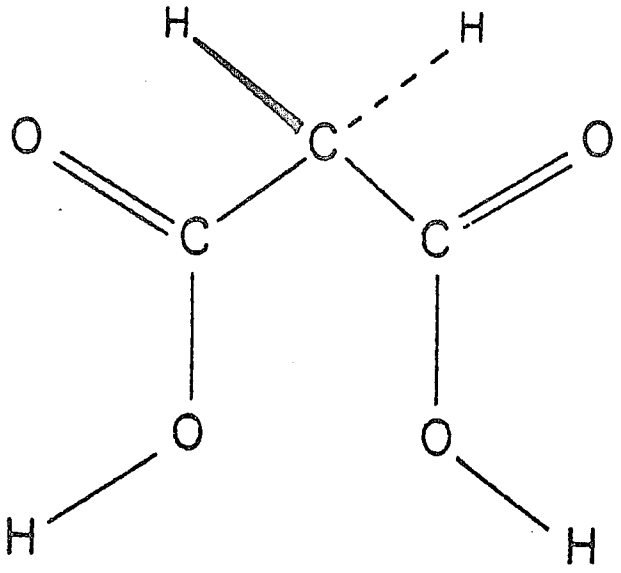
TABLE 3

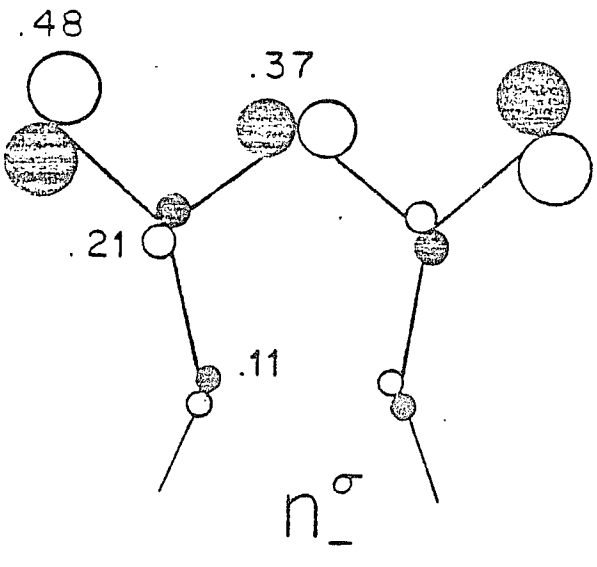
UPS DATA (in eV) AND ASSIGNMENTS FOR

β-DICARBOXYL COMPOUNDS

Number Index	Compounds	I(1)	I(2)	I(3)	I(4)
1.	Ethyl Malonate (EM)	10.84	11.38	~11.38	12.30
	MO type	n_-^σ	n_+^o	π_θ	$\pi_\oplus$
	Symmetry Designation	a"	a'	a"	a'
2.	Dimethyl Malonate (DMM)	10.55	11.12	~11.12	~11.12
	MO type	n_-^σ	n_+^o	$\pi_\oplus$	π_θ
	Symmetry Designation	b_2	a_1	b_1	a_2
3.	Diethyl Malonate (DEM)	10.36	10.96	~10.96	~10.96
	MO type	n_-^σ	n_+^o	$\pi_\oplus$	π_θ
	Symmetry Designation	b_2	a_1	b_1	a_2
4.	Diethyl Ethylmalonate (DEEM)	10.30	10.92	~10.92	~10.92
	MO type	n_-^σ	n_+^o	$\pi_\oplus$	π_θ
	Symmetry Designation	a"	a'	a"	a'
5.	Diethyl Diethylmalonate (DEDEM)	9.82	10.30	10.30	~10.92
	MO type	n_-^σ	n_+^o	$\pi_\oplus$	π_θ
	Symmetry Designation	b_2	a_1	b_1	a_2

Figure 5. Schematic representation of the n_-^{σ} and n_+^{o} MO's for malonic acid. LCAO MO coefficients are also shown. The CNDO/s[34] computation was performed for the X-ray diffraction geometry[35], altered in such a way as to accomodate a C_{2v} point-group symmetry.


H
H
O
C
C
O
O
O
H
H


.48
.37
.21
.11
n_-^σ

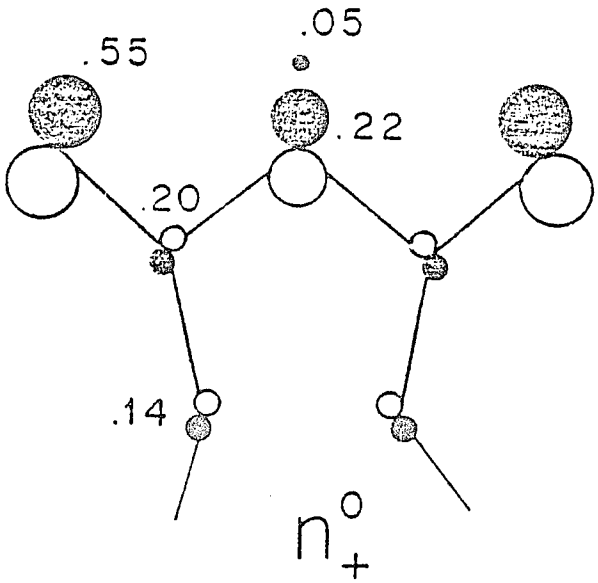

.05
.55
.22
.20
.14
n_+^o

TABLE 4

CALCULATED AND OBSERVED VALUES OF Δn (eV) FOR β-DICARBOXYL. COMPOUNDS

Number Index	Compound	Δn UPS	Δn CNDO/s	Δn CNDO/2
1.	Ethyl Malonate (EM)	0.54	1.28	1.43
2.	Dimethyl Malonate (DMM)	0.56	1.36	1.4
3.	Diethyl Malonate (DEM)	0.6	1.26	1.36
4.	Diethyl Ethylmalonate (DEEM)	0.57	1.12	0.75
5.	Diethyl Diethylmalonate (DEDEM)	0.48	1.05	1.29

observed values of Δn (where, $\Delta n = |I(n_-^{\sigma}) - I(n_+^{o})|$) is displayed in Figure 6.

The splitting of the $_0$ MO's, into $\pi_{\oplus}$ and π_{θ} components, is caused by "through-space" interactions.[31] However, the "through-space" interaction is rather weak because of the large separation of the carboxyl groups and, as a result, the $\pi_{\oplus}$ and π_{θ} orbitals are found to be almost degenerate. The $\pi_{\oplus}$ and π_{θ} MO's are schematized in Figure 7. An examination of the $\pi_{\oplus}$ and π_{θ} MO's indicate that π_{θ} should be more sensitive to esterification than $\pi_{\oplus}$ (since π_{θ} has larger amplitude on the -OH group). Thus, in ethyl malonate, $I(\pi_{\theta})$ should decrease whereas $I(\pi_{\theta})$ should remain more or less the same as in malonic acid.

RESULTS AND DISCUSSION

The UPS correlation diagram for EM, DMM, DEM, DEEM, ethyl formate (EF) and ethyl acetate (EA) is presented in Figure 8. The CNDO/s correlation diagram for EM, DMM, DEM, DEEM and diethyl diethyl malonate (DEDEM) is presented in Figure 9.

The low-energy UPS region (9-12eV) should contain two I(n) and two $I(\pi_0)$ event. One also expects that the HOMO should be of n type. This latter contention is supported by the totality of empirical studies on β-dicarbonyls[29], α-dicarbonyls[31], and virtually all available CNDO/2 and CNDO/s computations.[30,34] Furthermore, these same MO computations predict a near degeneracy of the $\pi_{\oplus}$ and π_{θ} MO's and confirm the preferential sensitivity, to which we have alluded previously, of the π_0 orbital towards esterification. Finally, a comparison of the UPS of the β-dicarboxyl with those of EF and EA provides a significant

Figure 6. Schematic representation of Δn for the β-dicarboxylic acid derivatives listed in Table 3. The numbers on the abscissa identify the compounds (See Table 3).

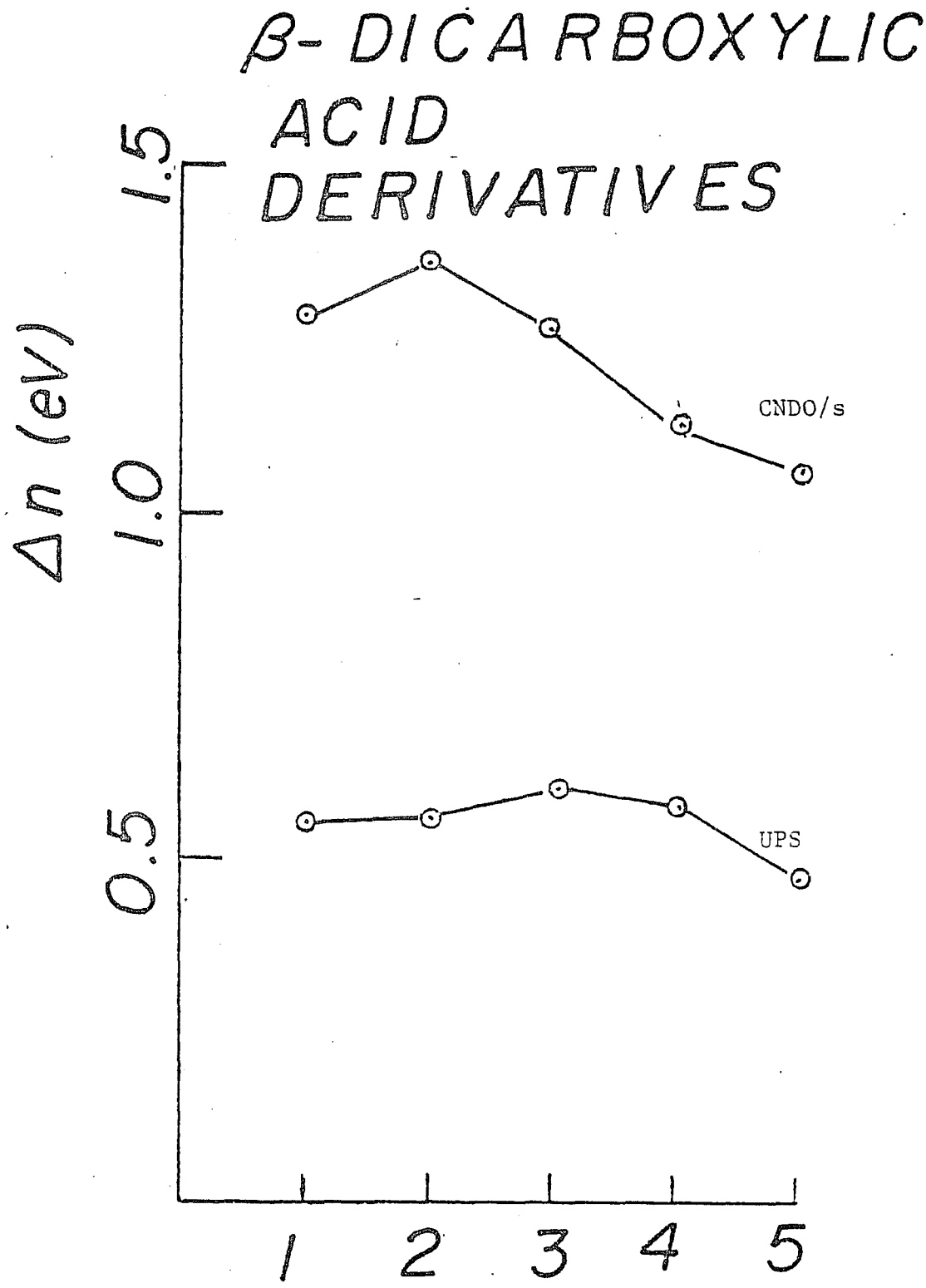
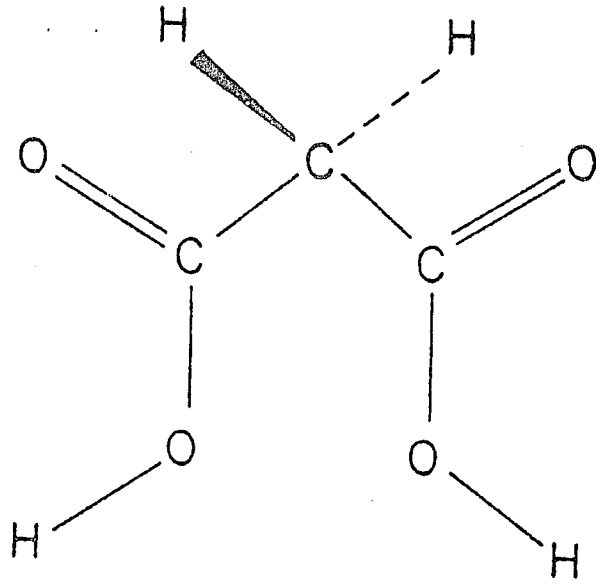
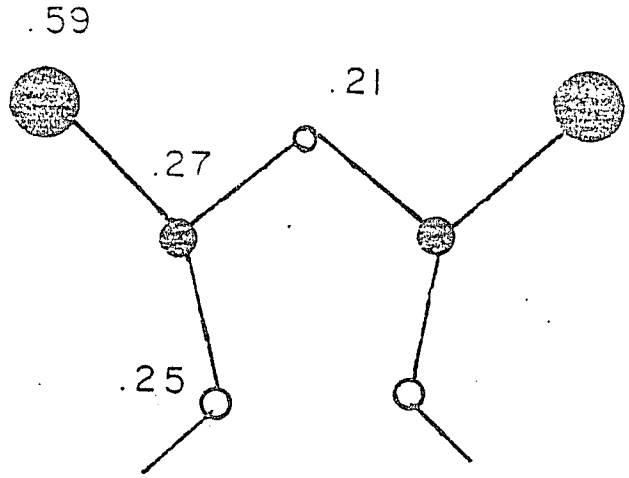
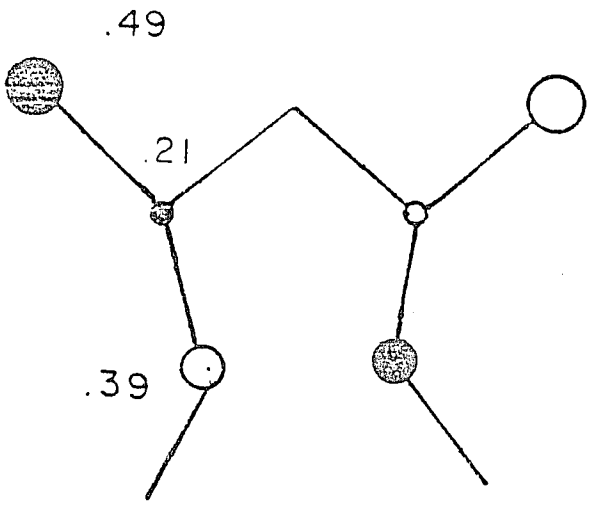

β-DICARBOXYLIC ACID DERIVATIVES
Δn (eV)
1.5
1.0
0.5
CNDO/s
UPS
1
2
3
4
5

Figure 7. Diagram of the π_{Φ} and π_{θ} MO's of malonic acid. Numbers above the lobes refer to MO coefficients. The CNDO/s[34] computation was performed at the X-ray diffraction geometry[35], altered in such a way as to accommodate a C_{2v} point group symmetry.





$\pi_{\oplus}$



$\pi_{\ominus}$

Figure 8. The UPS correlation diagram for EM, DMM, DEM, DEEM, DEDEM, EA and EF.

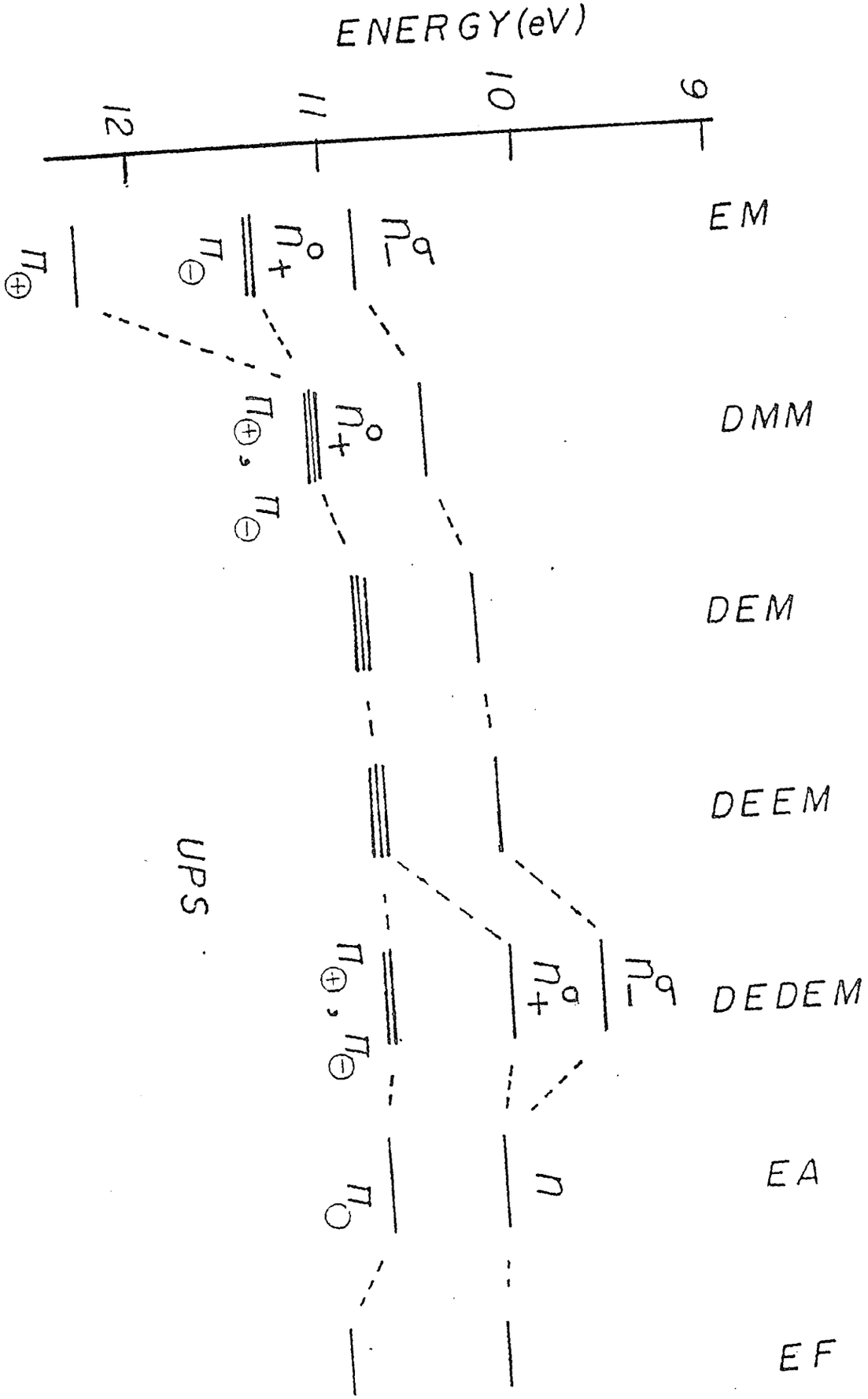

ENERGY(eV)
12
11
10
9
EM
DMM
DEM
DEEM
DEDEM
EA
EF
UPS

Figure 9. The CNDO/s correlation diagram for EM, DEM, DMM, DEEM and DEDMM.

ENERGY(eV)
12
11
10
9
$\pi_{\ominus}$
$\pi_{\oplus}$
σ_+
b_2
EM
$\pi_{\ominus}$
$\pi_{\oplus}$
DMM
DEM
DEEM
CNDO/s
DEDEM

vindication of all the above attitudes. Thus, with the above information at hand, the UPS analysis proceeds rather smoothly.

The first two low-energy UPS bands of EM exhibit an areal ratio of 1:2. Thus, I(1) = 10.84eV is assigned as $I(n_-^{\sigma})$. This assignment is consistent with the empirical prediction that $I(n_-^{\sigma}) < I(n_+^{o})$ in non-coaxial β-dicarbonyls[29], and with CNDO/s computations. Thus, the second band at 11.38eV must contain the $I(n_+^{o})$ event and one $I(\pi_0)$. Hence, the assignment of I(2) as $I(n_+^{o})$ yields $\Delta n = 0.5$eV, which agrees well with the general run of experiment for β-dicarbonyls.[29] The I(3) event at 11.38eV is assigned as $I(\pi_{\theta})$ of the OC_2H_5 group. The I(4) event is contained in the low-energy edge of the third broad UPS band and is assigned as $I(\pi_{\oplus})$ of the -OH group. The energy gap of ~1eV between $I(\pi_{\oplus})$ and $I(\pi_{\ominus})$ accords with that expected for a simple esterification.[36]

The low-energy UPS region of DMM, DEM, DEEM is characterized by two bands whose areal ratio is 1:3. Thus, in DMM, DEM and DEEM, I(1), which occurs at 10.55, 10.36, and 10.41eV, respectively, is assigned as $I(n_-^{\sigma})$. Consequently, I(2), which is contained in the second broad UPS band (which occurs at 11.12, 10.96 and 10.92eV in DMM, DEM and DEEM, respectively), is assigned as $I(n_+^{o})$. This assignment furnishes the order $n_-^{\sigma} > n_+^{o}$ and a split of ~0.5eV for the n MO's, in agreement with all empirical studies for β-dicarbonyls.[29] The CNDO/s computations support this same order. The I(3) and I(4) events, which also occur in this second broad UPS band, are assigned as $I(\pi_{\oplus})$ and $I(\pi_{\ominus})$, respectively. This assignment is consistent with the weak "through-space" interactions expected for the π_0 MO's of the β-dicarboxylic acid compounds, and with the results of CNDO/s computations which place

the n_+^o, π_θ and $\pi_\oplus$, MO's within a narrow range of 0.4eV. Finally, a comparison of the UPS of DEM with those of EF and EA, on the basis of composite molecule approach, validates the assignments made above.

In DEDEM, I(1), which occurs in the first UPS band at 9.82eV, is assigned as $I(n_-^\sigma)$. Thus, the assignment of I(2), which is contained in the second band at 10.3CeV, as $I(n_+^o)$ accords with the expected order and splitting of n MO's. I(3) and I(4) which occur in the third broad UPS band at 10.92eV are assigned as $I(\pi_\oplus)$ and (π_θ). These assignments are consistent with the relative areas under these two bands. The CNDO/s results for DEDEM support this assignment.

In going from DEEM to DEDEM, the $\pi_\oplus$ and π_θ MO's remain unaltered at 10.92eV whereas the n_-^σ and n_+^o MO's experience a substantial shift. This behavior conforms to the fact that the n MO's are more sensitive to the changes in the substituent at the carbonyl carbon.[36]

γ - DICARBOXYL COMPOUNDS: The UPS of succinic acid (SA), succinamic acid (SMA), monomethyl succinate (MS), dimethyl succinate (DMS) and dimethyl methylsuccinate (DMMS) are displayed in Figure 10. The ionization events and their assignments are tabulated in Table 5. The UPS correlation diagram for SA, SMA, MS, DMS, DMMS, acetic acid (AA), methyl acetate (MA), and acetamide (AM) is displayed in Figure 11. Figure 11 also constitutes a CNDO/s[34] correlation diagram for SA, SMA, MS, DMS and DMMS.

The following considerations facilitate UPS assignments:

- --- In these compounds, the low-energy UPS region (i.e., 9-12eV) should contain two I(n) and two $I(\pi_0)$ events. However, since the carboxyl groups are now quite far apart, "through-bond" interaction

Figure 10. UPS of SA, SMA, MS, DMS and DMMS.

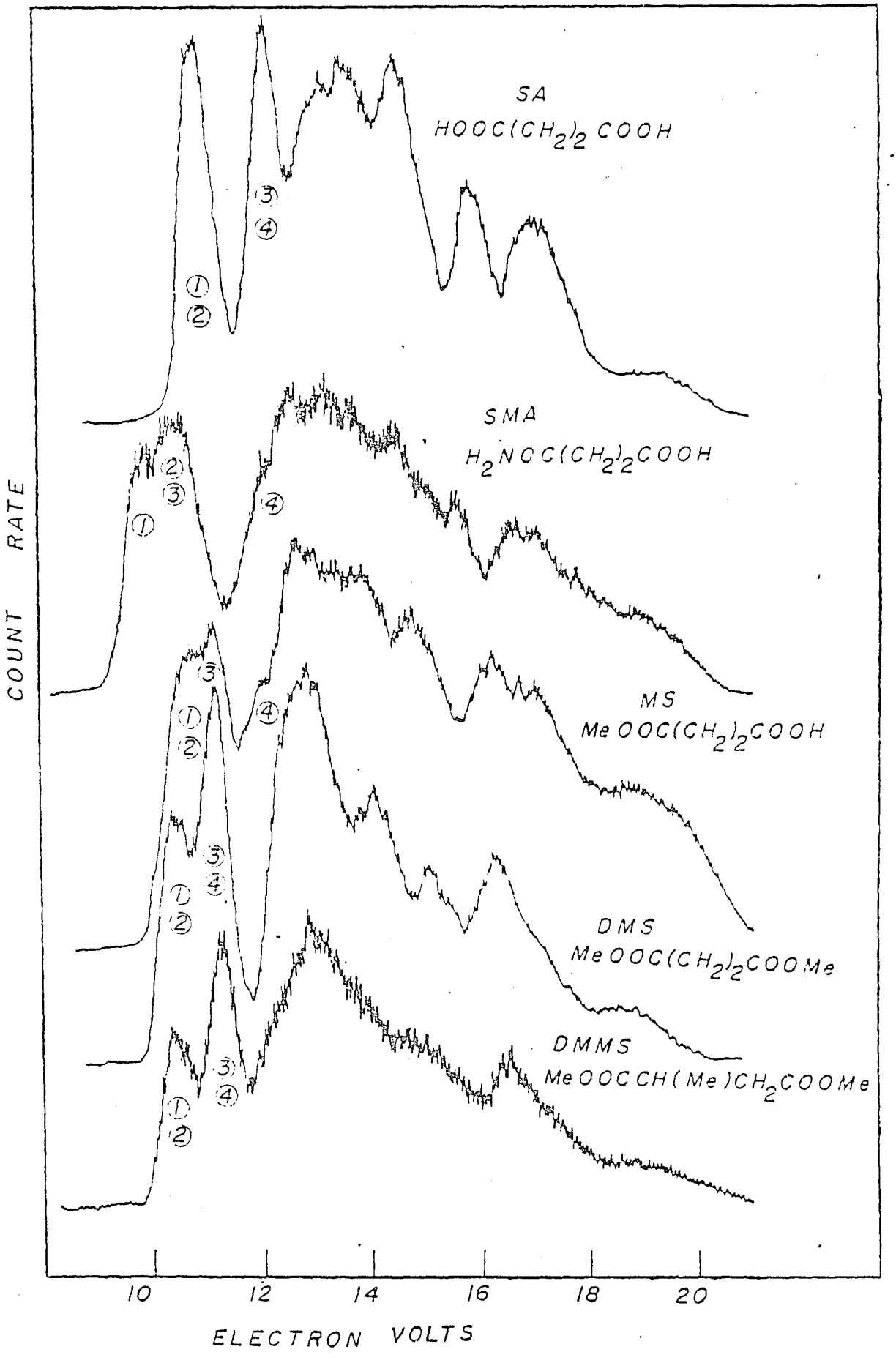

SA
HOOC(CH2)2COOH
SMA
H2NOC(CH2)2COOH
MS
MeOOC(CH2)2COOH
DMS
MeOOC(CH2)2COOMe
DMMS
MeOOCCH(Me)CH2COOMe
COUNT RATE
10
12
14
16
18
20
ELECTRON VOLTS

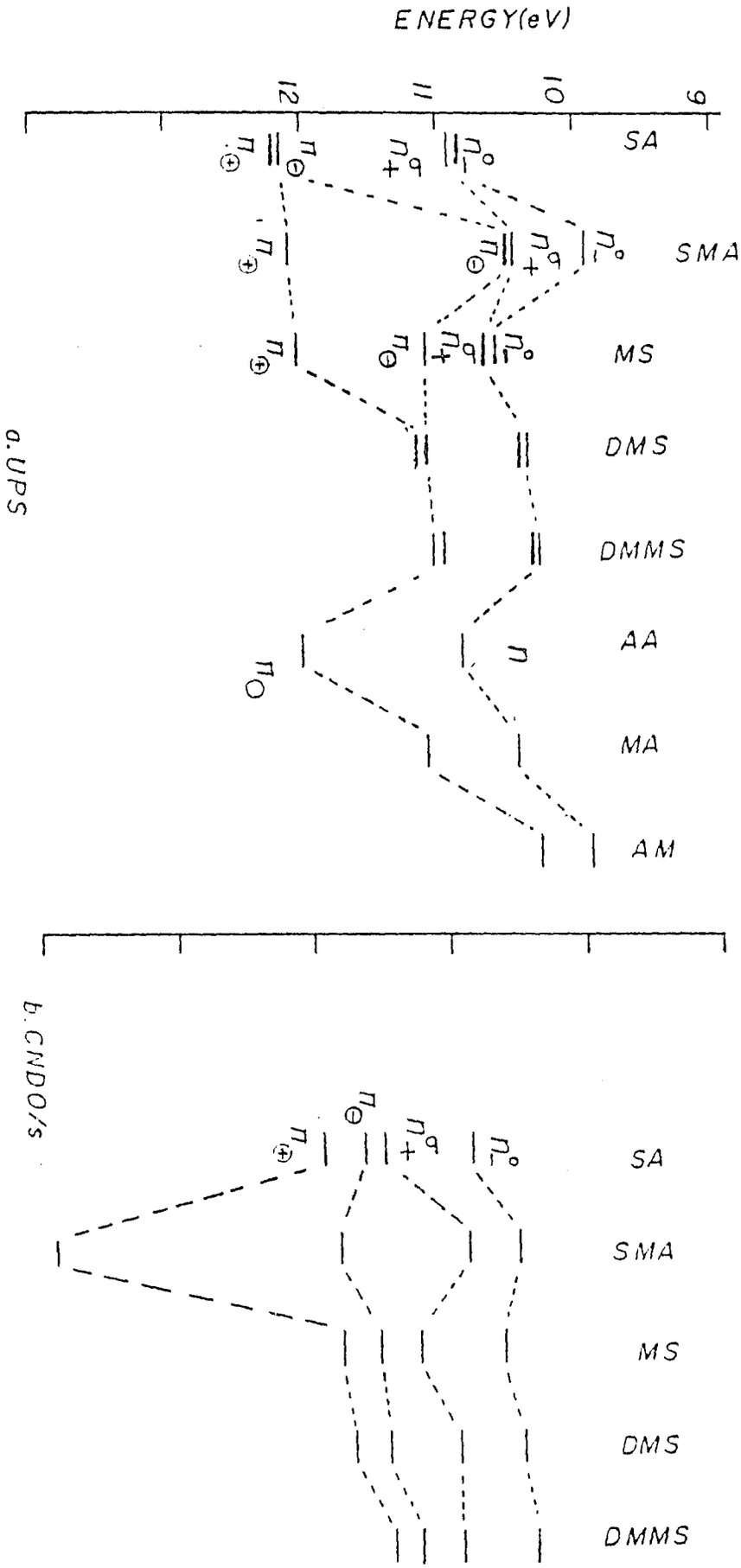
TABLE 5

UPS DATA (in eV) AND ASSIGNMENTS FOR

γ-DICARBOXYL COMPOUNDS

Number Index	Compounds	I(1)	I(2)	I(3)	I(4)
1.	Succinic Acid (SA)	10.92	10.92	12.15	12.15
	MO type	n_-^o	n_+^σ	π_θ	$\pi_\oplus$
2.	Succinamic Acid (SMA)	9.92	10.46	10.46	12.11
	MO type	$n_-^{o'}$	n_+^σ	π_θ	$\pi_\oplus$
3.	Monomethyl Succinate (MS)	10.67	10.67	11.11	12.04
	MO type	n_-^o	n_+^σ	π_θ	$\pi_\oplus$
4.	Dimethyl Succinate (DMS)	10.37	10.37	11.12	11.12
	MO type	n_-^σ	n_+^σ	π_θ	$\pi_\oplus$
5.	Dimethyl Methyl-succinate (DMMS)	10.31	10.31	11.07	11.07
	MO type	n_-^o	n_+^σ	π_θ	$\pi_\oplus$

Figure 11. The UPS and CNDO/s correlation diagrams for SA, SMA, MS, DMS, DMMS, AA, MA and AM.


ENERGY(eV)
12
11
10
9
SA
SMA
MS
DMS
DMMS
AA
MA
AM
a. UPS
b. CNDO/s

should be negligible and, as a result, $I(n_+^{\sigma})$ and $I(n_-^{o})$ should be nearly degenerate.[29] Moreover, in these compounds where the carboxyl groups are coaxial, empirical studies predict the order $I(n_-^{o}) < I(n_+^{\sigma})$.[29] CNDO/s computations confirm these predictions.

- - - The "through-space" interaction which is the cause of the removal of the degeneracy of the π_0 MO's should also be very weak.[31] Consequently, the $I(\pi_{\oplus})$ and $I(\pi_{\ominus})$ events are expected to be almost degenerate.

- - - In view of the large carboxyl group separation, these molecules may be suppoede to consist of two monocarboxyl components. Hence, the UPS assignment for these compounds is facilitated by comparison with the UPS of AA, MA and AM. The UPS analysis may now be performed.

The first two UPS bands of SA, which occur at 10.92 and 12.15eV, respectively are equally intense. Thus, the I(1) and I(2) events, which we suppose to be contained in the first UPS band are assigned as $I(n_-^{o})$ and $I(n_+^{\sigma})$, respectively. The width of this first band is adequate to encompass a $\Delta I(n)$ splitting of ~0.3eV (i.e., the split expected for γ-dicarbonyls[29]). Furthermore, these values of $I(n_-^{o})$ and $I(n_+^{\sigma})$ compare favorably with I(n) for acetic acid at 10.84eV. The I(3) and I(4) events, which occur in the second UPS at 12.15eV, are assigned as $I(\pi_{\ominus})$ and $I(\pi_{\oplus})$ events, respectively. These assignments are consistent with the fact that $I(\pi_0)$ of AA occurs at 12.05eV. Furthermore, the UPS MO order $\pi_{\oplus} < \pi_{\ominus} < n_+^{\sigma} < n_-^{o}$ is reproduced by CNDO/s computations.

In SMA, the I(1), I(2), I(3) events are contained in the first

two UPS bands, the areal ratio of which appears to be approximately 1:2. The I(4) event, along with other unidentified ionization events, occurs in the third broad UPS band. Thus, I(1) = 9.92eV is assigned as $I(n_-^o)$. The I(2) and I(3), which lie at 10.46 eV are assigned as $I(n_+^\sigma)$ and $I(\pi_\theta)$, respectively. This assignment yields a value of $\Delta I(n) \sim 0.54$eV which is in reasonable agreement with empirical studies on other γ-dicarbonyls. Thus, the I(4) event, which occurs at 12.04eV, is assigned as $I(\pi_\oplus)$. The separation of the $I(\pi_\theta)$ and $I(\pi_\oplus)$ events, is 1.63eV, which accords with the expected shift of the π_0 ionization caused by amination of the carbonyl group. Finally, a comparison of the spectrum of SMA with those of AA and AM, on the basis of a "composite-molecule" approach, validates these assignments. The CNDO/s results also support the same ordering of MO's, namely $n_-^o > n_+^\sigma > \pi_\theta > \pi_\oplus$.

In MS, the I(1) and I(2) events occur in the first UPS band at 10.17eV and are assigned as $I(n_-^o)$ and $I(n_+^\sigma)$, respectively. The I(3) event is contained in the second UPS band at 11.11eV and is assigned as $I(\pi_\theta)$. This assignment is consistent with the areal ratio, 2:1, of these tow bands. Thus, the I(4) event, which is present in the rather broad third UPS band, is assigned as $I(\pi_\oplus)$. Such an analysis is intuitive, since the π_θ and $\pi_\oplus$ MO's have rather large amplitudes on the $-OCH_3$ and -OH groups, respectively. Finally, the shift of ~1eV in $I(\pi_\theta)$ in going from SA to MS is comparable with the susceptibility of the π_0 MO towards perturbations introduced by esterification. The above assignment scheme is also supported by a comparison of the spectrum of MS with those of AA and MA. The CNDO/s results constitute further validation of the above assignments.

The first two UPS bands of DMS, which are equally intense, are

supposed to contain two I(n) and two I(π_0) events, respectively. Thus the I(1) and I(2) events, which occur at 10.37eV are assigned as I(n_-^o) and I(n_+^σ), respectively. The I(3) and I(4) events, which occur at 11.12eV, are assigned as I(π_θ)and I($\pi_\oplus$), respectively. The shift of I(π_θ) between SA and DMS, ΔI ~1.03eV, is in the expected range for esterification effects on a π_0 MO.[36] The shift of the first UPS band between the same two compounds, ΔI ~0.55eV, also accords with the expected esterification effect for n MO's.[31] These assignments are validated by CNDO/s results and by "composite-molecule" approaches based on the comparison of the UPS of DMS and MA.

The UPS of DMMS is very similar to that of DMS. The attachment of a CH_3 group to the skeletal C-atom apparently has very little effect on either the n or π_0 MO's. Thus the UPS of DMS is readily analyzed.

δ-Dicarboxyl Compounds: In the non-coaxial δ-dicarboxyls, the n MO order should be $n_-^\sigma > n_+^o$, as it is in the non-coaxial β-dicarboxyls.

Figure 12 displays the UPS of glutaric acid (GA), dimethyl glutarate (DMG) and monomethyl glutarate (MMG). The ionization events and their assignments are tabulated in Table 6. The UPS correlation diagram for GA, MMG, MDG, propionic acid (PA)[37] and acetic acid (AA) is given in Figure 13. The CNDO/2 correlation diagram for GA, MMG and DMG is presented in Figure 13.

The "through-bond " interactions between n orbitals and the "through-space" interactions between π_0 orbitals are expected to be very weak because the carboxyl groups are separated by three carbon atoms. Consequently, the n MO's should be more or less degenerate, and this also should be the case for the π_0 MO's.

Figure 12. UPS of GA, DMG, and MMG.

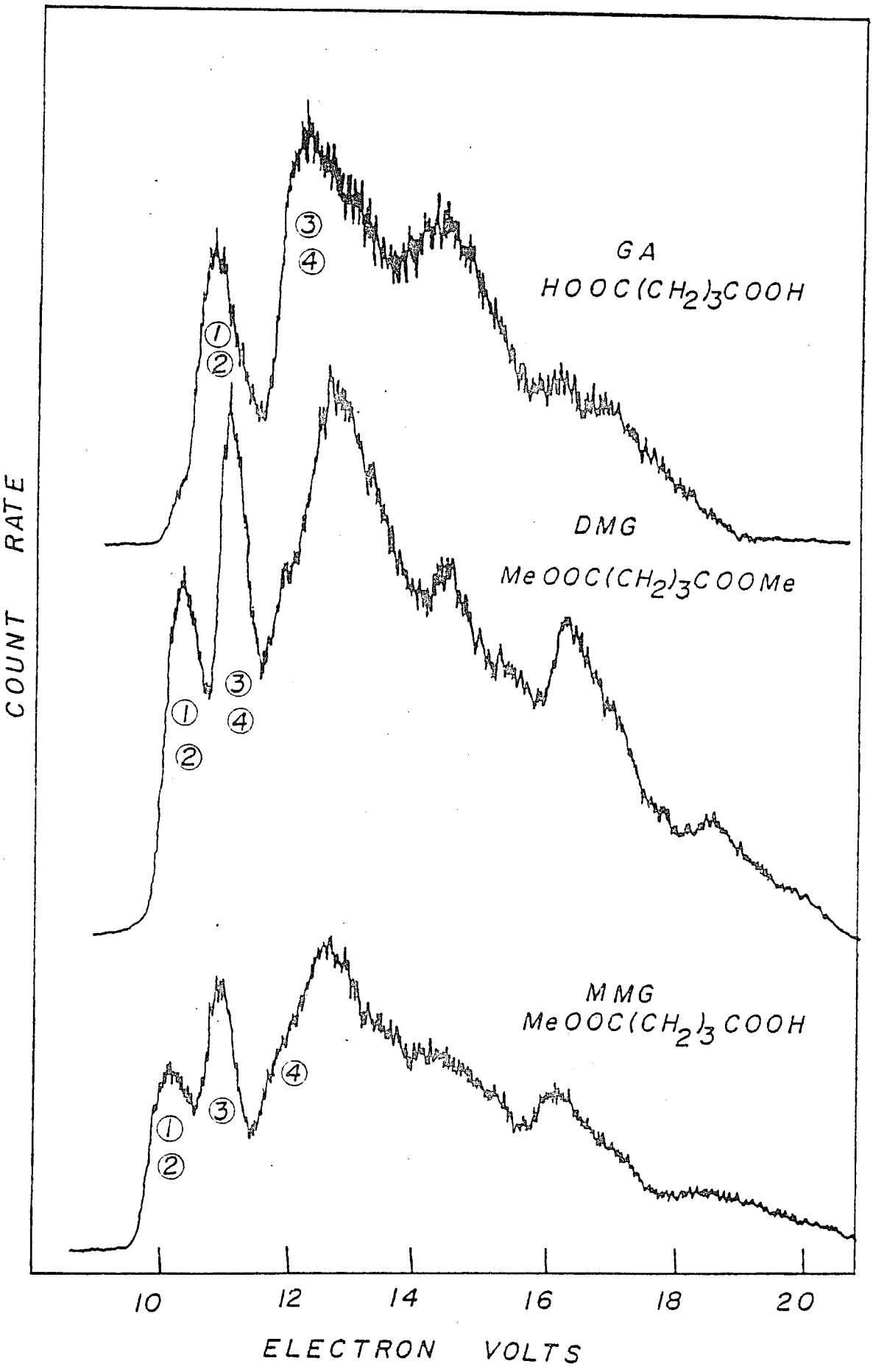

GA
HOOC(CH2)3COOH
DMG
MeOOC(CH2)3COOMe
MMG
MeOOC(CH2)3COOH
1
2
3
4
COUNT RATE
10
12
14
16
18
20
ELECTRON VOLTS

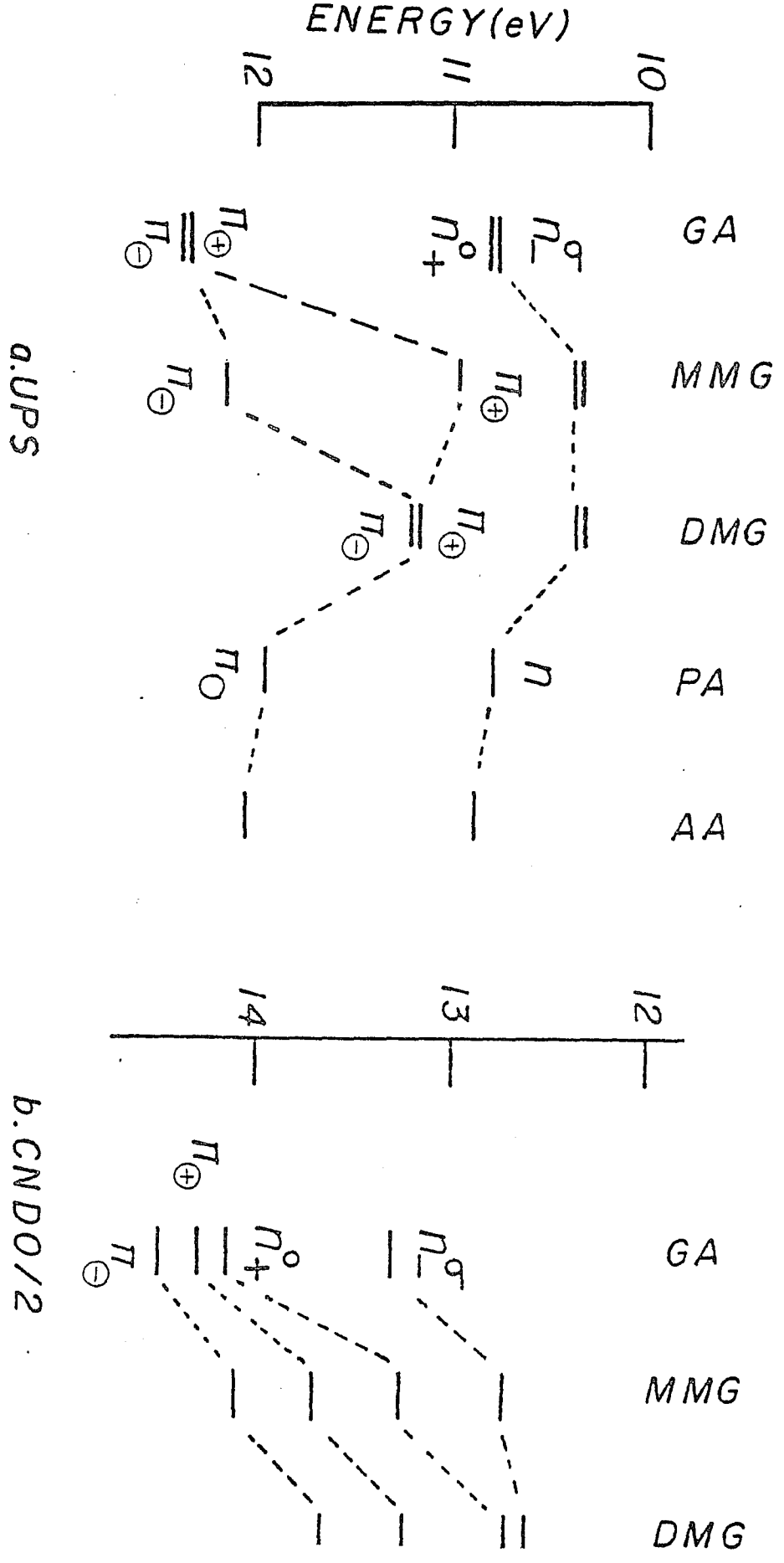
TABLE 6

UPS DATA (in eV) AND ASSIGNMENTS FOR

δ-DICARBOXYL COMPOUNDS

Number Index	Compounds	I(1)	I(2)	I(3)	I(4)
1.	Glutaric Acid (GA)	10.76	10.76	12.33	12.33
	MO type	n_-^σ	n_+^o	$\pi_\oplus$	$\pi_\ominus$
2.	Monomethyl Glutarate (MMG)	10.2	10.2	10.95	12.2
	MO type	n_-^σ	n_+^o	$\pi_\oplus$	$\pi_\ominus$
3.	Dimethyl Glutarate	10.36	10.36	11.14	11.14
	MO type	n_-^σ	n_+^o	$\pi_\oplus$	$\pi_\ominus$

Figure 13. The UPS and CNDO/2 correlation diagrams for GA, MMG, DMG, PA and AA.


ENERGY(eV)
12
11
10
a.UPS
GA
MMG
DMG
PA
AA
14
13
12
b.CNDO/2
GA
MMG
DMG

The first two UPS bands of GA and DMG are equally intense. Consequently I(1) and I(2) of GA and DMG, which are supposed to coincide in the first UPS band, are assigned as $I(n_-^{\sigma})$ and $I(n_+^{o})$, respectively. The second band of GA and DMG contains the I(3) and I(4) events. Consequently, I(3) and I(4) are assigned as $I(\pi_{\oplus})$ and $I(\pi_{\theta})$. The width of the first band is adequate to encompass a $\Delta I(n)$ splitting of ~0.1eV (i.e., that expected for δ-dicarbonyls[29]). The cited n-MO order, $n_-^{\sigma} > n_+^{o}$, is also confirmed by CNDO/2 computations. The shift of the π_0 MO between GA and DMG is 1.2eV which agrees well with the expected magnitudes of such a shift for an $I(\pi_0)$ MO.[31,36]

In MMG, the first two UPS bands possess an areal ratio of approximately 2:1. Hence, the I(1) and I(2) events which are supposed to occur in the first UPS band at 10.2eV are assigned as $I(n_-^{\sigma})$ and $I(n_+^{0})$, respectively. The I(3) event occurs in the second UPS band at 10.95eV and is assigned as $I(\pi_{\oplus})$. The I(4) event is present in a rather broad third UPS band at 12.2eV and is assigned as $I(\pi_{\theta})$. This assignment is consistent with the fact that the $\pi_{\oplus}$ and π_{θ} MO's have rather large amplitudes on the OCH_3 and -OH groups, respectively. Morever, the difference $I(\pi_{\oplus}) - I(\pi_{\theta})$ ~1.25eV accords well with that expected for the effects of esterification on a π_0 MO.

Comparison of the spectra of GA, DMG and MMG with those of PA supports the above assignments. Although, the MO order is mimicked by CNDO/2 results, quantitive agreement is lacking. However, this may be an oddity of the CNDO/2 computation, which also overestimates[38] the orbital energies by ~3eV.

ε-Dicarboxyl Compounds. It can be assumed, in view of the large separation of the carboxyl centers, that the two n-ionization events (and

the two π_0 ionization events) are effectively degenerate. The UPS of adipic acid (ADA), monomethyl adipate (MMADA), and diethyl adipate (DEADA) are displayed in Figure 14. The UPS data and their assignments are presented in Table 7.

The UPS correlation diagram for ADA, MMADA, DEADA and propionic acid (PA) and the CNDO/s correlation diagram for ADA, MMADA and DEADA is shown in Figure 15.

In ADA, the first two bands, which occur at 10.67 and 12.07eV respectively, are equally intense. Thus, the I(1) and I(2) events, which are contained in the first UPS band, are assigned as $I(n_-^o)$ and $I(n_+^\sigma)$. This assignment is consistent with the predicted n-MO order of $n_-^o > n_+^\sigma$ for coaxial ϵ-dicarboxyl compounds.[29] The I(3) and I(4) events, which occur in the second band, are assigned as $I(\pi_\oplus)$ and $I(\pi_\ominus)$. This assignment is consistent with the CNDO/s computed results and with the "composite-molecule" approach involving comparison of the spectrum of ADA with that of PA.

In MMADA, the I(1) and I(2) events, which occur in the first band at 10.62eV, are assigned as $I(n_-^o)$ and $I(n_+^\sigma)$. This assignment is consistent with the assignment of the n MO's in ADA. The I(3) ionization event, which occurs in the second band at 11.15eV, is assigned as $I(\pi_\oplus)$. This assignment is based on the supposition that the $\pi_\oplus$ MO has substantially larger amplitude on the $-OCH_3$ group than does the $\pi_\ominus$ MO. The I(4) event which occurs in a rather diffuse third band at 12.0eV, is assigned as $I(\pi_\ominus)$. This yields a shift of ~1eV for $I(\pi_\ominus)$ event upon going from ADA to MMADA, which accords with the expected shift of an $I(\pi_\ominus)$ event caused by esterficiation.[31] This assignment is validated by the fact that the $\pi_\ominus$ MO appears to possess

Figure 14. UPS of ADA, MMADA and DEADA.

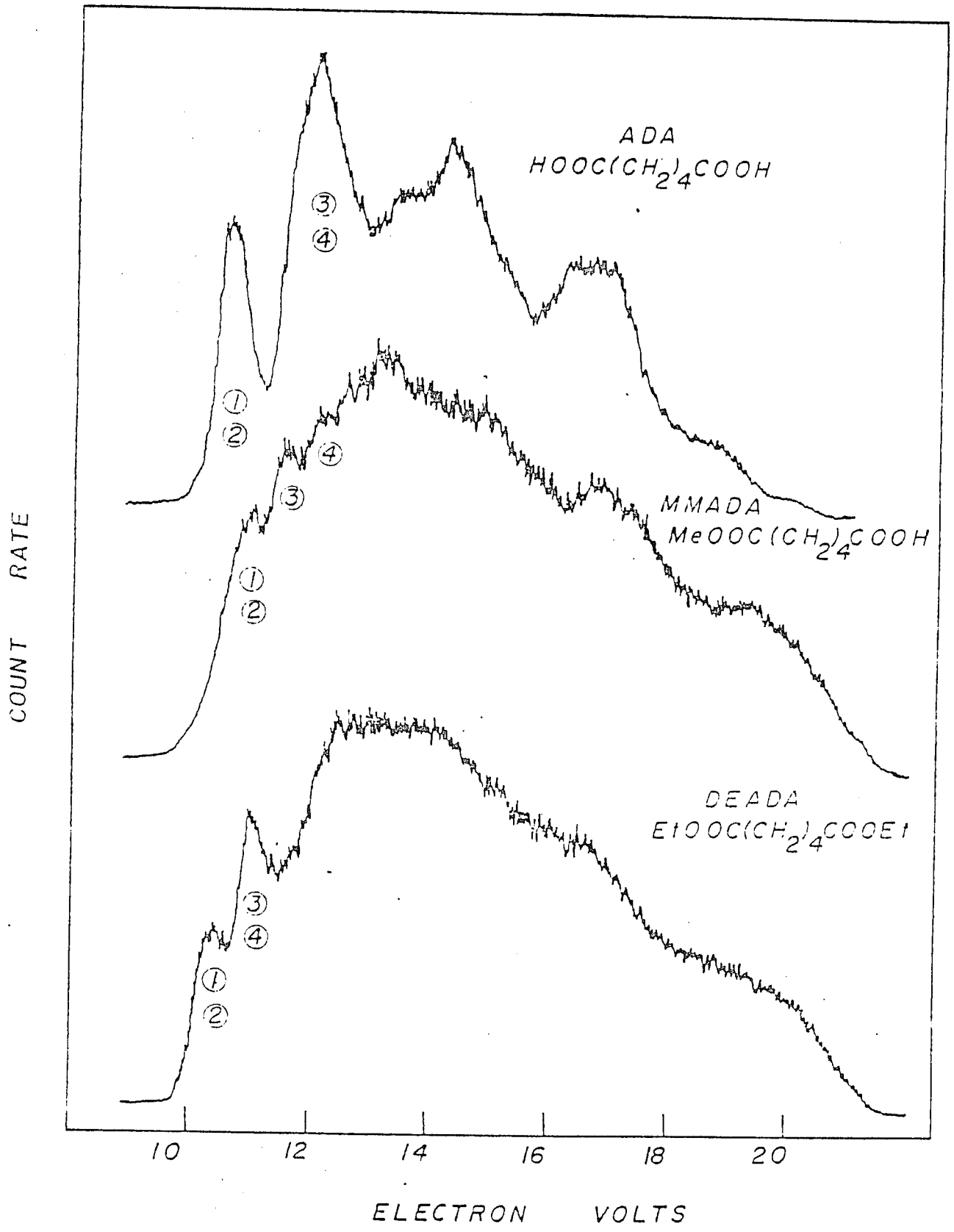

ADA
HOOC(CH2)4COOH
MMADA
MeOOC(CH2)4COOH
DEADA
EtOOC(CH2)4COOEt
①
②
③
④
COUNT RATE
10
12
14
16
18
20
ELECTRON VOLTS

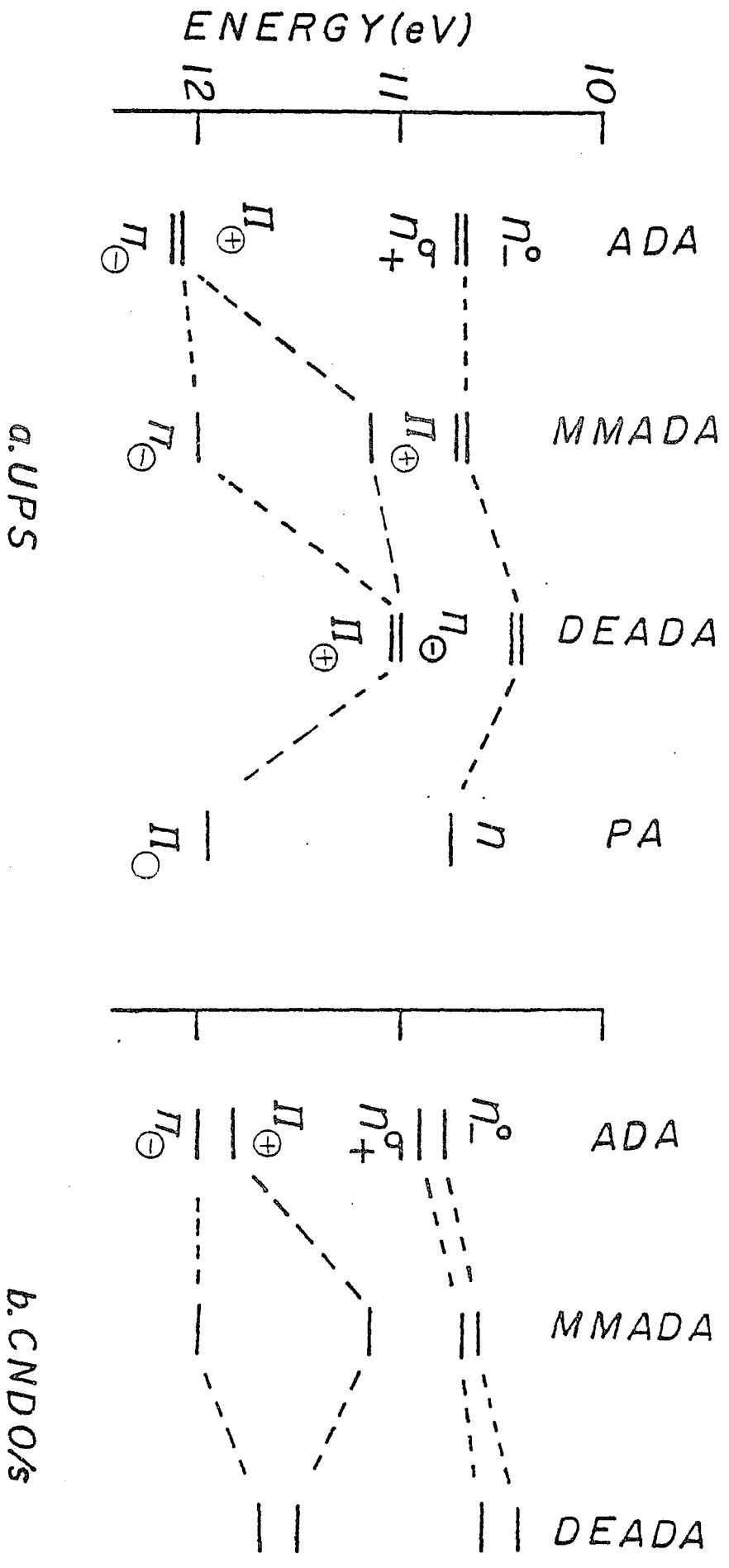
TABLE 7

UPS DATA (in eV) AND ASSIGNMENTS FOR

ω-DICARBOXYL COMPOUNDS

Number Index	Compounds	I(1)	I(2)	I(3)	I(4)
1.	Adipic Acid (ADA)	10.67	10.67	12.07	12.07
	MO type	n_-^o	n_+^σ	$\pi_\oplus$	$\pi_\ominus$
2.	Monomethyl Adipate (MMADA)	10.67	10.67	11.15	12.0
	MO type	n_-^o	n_+^σ	$\pi_\oplus$	$\pi_\ominus$
3.	Diethyl Adipate (DEADA)	10.4	10.4	11.0	11.0
	MO type	n_-^o	n_+^σ	$\pi_\oplus$	$\pi_\ominus$

Figure 15. The UPS and CNDO/s correlation diagrams for ADA, MMADA, DEADA and PA.


ENERGY(eV)
12
11
10
ADA
MMADA
DEADA
PA
a. UPS
b. CNDO/s

substantially larger amplitude on the -OH group than does the $\pi_{\oplus}$ MO.

In DEADA, two equally-intense bands occur at 10.4eV and 11.0eV respectively. The I(1) and I(2), events which occur in the first UPS band at 10.4eV are assigned as $I(n_-^o)$ and $I(n_+^\sigma)$ respectively. The I(3) and I(4) events, which are contained in the second UPS band, are assigned as $I(\pi_{\oplus})$ and $I(\pi_{\ominus})$. In going from ADA to DEADA, the $I(\pi_{\ominus})$ event shifts by ~1eV. This shift is in the range expected for the effect of esterification on a π_0 ionization event.[31] Finally, the CNDO/s results reproduce the MO order $n_-^o > n_+^\sigma > \pi_{\oplus} > \pi_{\ominus}$.

CONCLUSION

This work summarizes and analyses the UPS results for β-, γ-, δ- and ε-dicarboxylic acids and derivatives. Apart from the assignment of UPS, the salient features of this work are as follows:

(i) The "through-bond" nature of the interaction involving n-MO's in dicarboxyl compounds is utilized to explain the UPS of β-, γ-, δ- and ε-dicarboxylic acids and derivatives.

(ii) The "through-space" interaction between π_0 MO's in these compounds is invoked in order to explain their UPS.

(iii) The effect of O-alkylation (i.e., esterification) on the π_0-MO is confirmed.

(iv) It has been shown that the "composite-molecule" approach can be used to validate the assignments made on the basis of other interpretive criteria.

CHAPTER THREE

ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY OF PHOSPHORUS COMPOUNDS

INTRODUCTION

Although phosphorus compounds are ubiquitous in the biological realm, very little UPS work has been invested in them. The phosphorus trihalides[39,40] and phosphoryl trihalides[41-47] have been the subject of extensive theoretical and experimental studies. However, the UPS of phosphites and phosphates, though subject to some preliminary work,[48] appears to have been largely neglected.

Koopmans' Theorem,[3] in conjunction with UPS data, provides a very direct test of the quality of quantum mechanical computations.[49] Consequently, the scope of this work will be limited to the following considerations:

(i) To obtained UPS data for organic phosphites, phosphates and structurally-related compounds.

(ii) To compare the UPS data so obtained with the previously available data and with quantum mechanical calculations in order to arrive at a consistent set of UPS assignments.

(iii) To compare the UPS of phosphates and substituted phosphates in order to discern substitution and symmetry-breaking effects.

I. EXPERIMENTAL AND COMPUTATIONAL

He I UPS were recorded with a Perkin-Elmer PS-18 photoelectron spectromoter with a 10-cm radius cylindrical electrostatic field deflection analyzer. The ionization energy was provided by the 584Å (21.22eV) He I resonance line. The ejected electrons were detected by a Bendix "Channeltron" electron multiplier. The $2p_{1/2}$ and $2p_{3/2}$ lines of Xe and Ar were used to calibrate the spectra with regard to both energy and resolution. The resolution prior to each run was in the range 20-25 meV.

Trimethyl phosphite (TEPI), triethyl phosphites (TEPI), trimethyl phosphate (TMPA), triethyl phosphate (TEPA) and dimethyl methylphosphonate (DMMPNA) were purified by vacuum distillation. Handling of diethyl dithiophosphate (DEDTPA), diethyl chlorothiophosphate (DECLTPA) and diethyl chlorophosphate (DECLPA) involved the use of an air-tight glove box filled with nitrogen.

Quantum mechanical calculations were performed in the QCPE 141-CNDO/2 alogrithmic mode.[34] For calculations on TEPI, the equilibrium geometrical parameters obtained by gaseous electron diffraction techniques[50] were used. Calculations on all other molecules were performed for the most stable conformation[51] with standard bond lengths and bond angles[52] as geometrical parameters.

II. RESULTS AND DISCUSSION

The compounds studied in this work can be divided into three categories:

(i) Phosphites

(ii) Phosphates

(iii) Substituted phosphates

Since the phosphites are the least complicated among these three, their spectra will be discussed first, to be followed, in turn, by a discussion of phosphates and substituted phosphates.

A. Phosphites. The UPS of TMPI and TEPI are displayed in Figure 1. Ionization events and their assignments are tabulated in Table 1. Since, these molecules can be categorized in the C_{3v} point group, their MO's are labelled a_1, a_2, and e. This labelling facilitates correlation with the corresponding data set for the phosphorus trichloride (PTCL). The UPS correlation diagram for TMPI, TEPI and PTCL is displayed in Figure 2.

The CNDO/2 MO correlation diagram is also shown in Figure 2. Phosphorus trichloride is not included in this latter diagram because the CNDO/2 method 40 does not reproduce the UPS MO order for PTCL. However, for the sake of completeness, the UPS,[39a,39b,39c,40,47,48] CNDO/2,[40] HMO (Extended Hückel)[40] and ab initio[43,44] results for PTCL are collected in Figure 3. A close examination of Figure 3 leads to the following comments:

(i) While the ab initio computation reproduces the experimental MO order, it understimates the energy of the first ionization event in PTCL.

(ii) The CNDO/2 method reverses the order of the $1a_2$ and 4e MO's. Moreover, it overestimates the ionization energies.

(iii) The HMO method reverses the order of $1a_2$ and 4e MO's. It also fails to reproduce the energy gap between the various ionization events.

The accepted MO order in PTCL is $4a_1 > 1a_2 > 4e > 3e > 3a_1$. The nature and characteristics of these MO's are outlined in Table 1.

The low-energy UPS region of the phosphites (9-15eV) contains

FIGURE 1. UPS of TMPI and TEPI

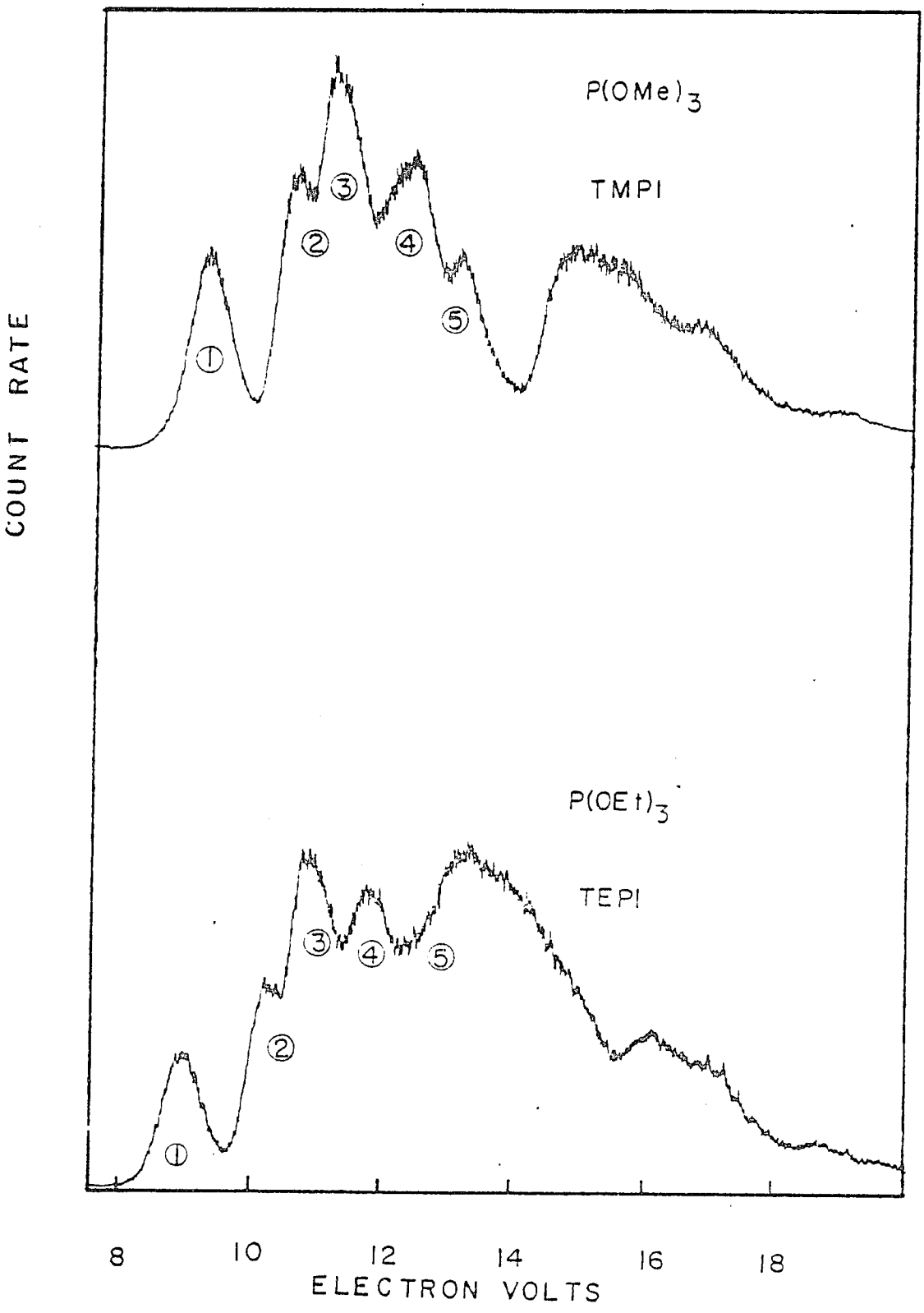

P(OMe)3
TMPI
①
②
③
④
⑤
P(OEt)3
TEPI
①
②
③
④
⑤
COUNT RATE
8
10
12
14
16
18
ELECTRON VOLTS

TABLE 1

UPS DATA (in eV) AND ASSIGNMENTS FOR

PHOSPHORUS TRICHLORIDE AND PHOSPHITES

Number Index	Compounds	I(1)	I(2)	I(3)	I(4)	I(5)
1.	Phosphorus Trichloride (PTCL)[a]	10.52	11.70	12.00	12.97	14.23
	MO type	P-lone pair	Cl-lone pair	Cl-lone pair	strongly bonding	P-Cl bonding
	Symmetry Designation[b]	$4a_1$	$1a_2$	4e	3e	$3a_1$
2.	TMPI	9.30	10.63	11.29	12.42	13.12
	MO type	P-lone pair	O-lone pair	O-lone pair	strongly bonding	P-O bonding
	Symmetry Designation	a_1	a_2	e	e	a_1[c]
3.	TEPI	8.90	10.23	10.79	11.75	12.85
	MO Type	P-lone pair	O-lone pair	O-lone pair	strongly bonding	P-O bonding
	Symmetry Designation	a_1	a_2	e	e	a_1

a. Taken from Ref. 1a, 1b, 2 and 9.

b. The outer valence electronic configuration is the same as in Ref. 9.

c. Part of the broad composite band, which also contains C-C, C-O and C-H σ ionization events.

Figure 2. The UPS correlation diagram for TMPI. TEPI and PTCL. and a CNDO/2 correlation diagram for TMPI and TEPI.

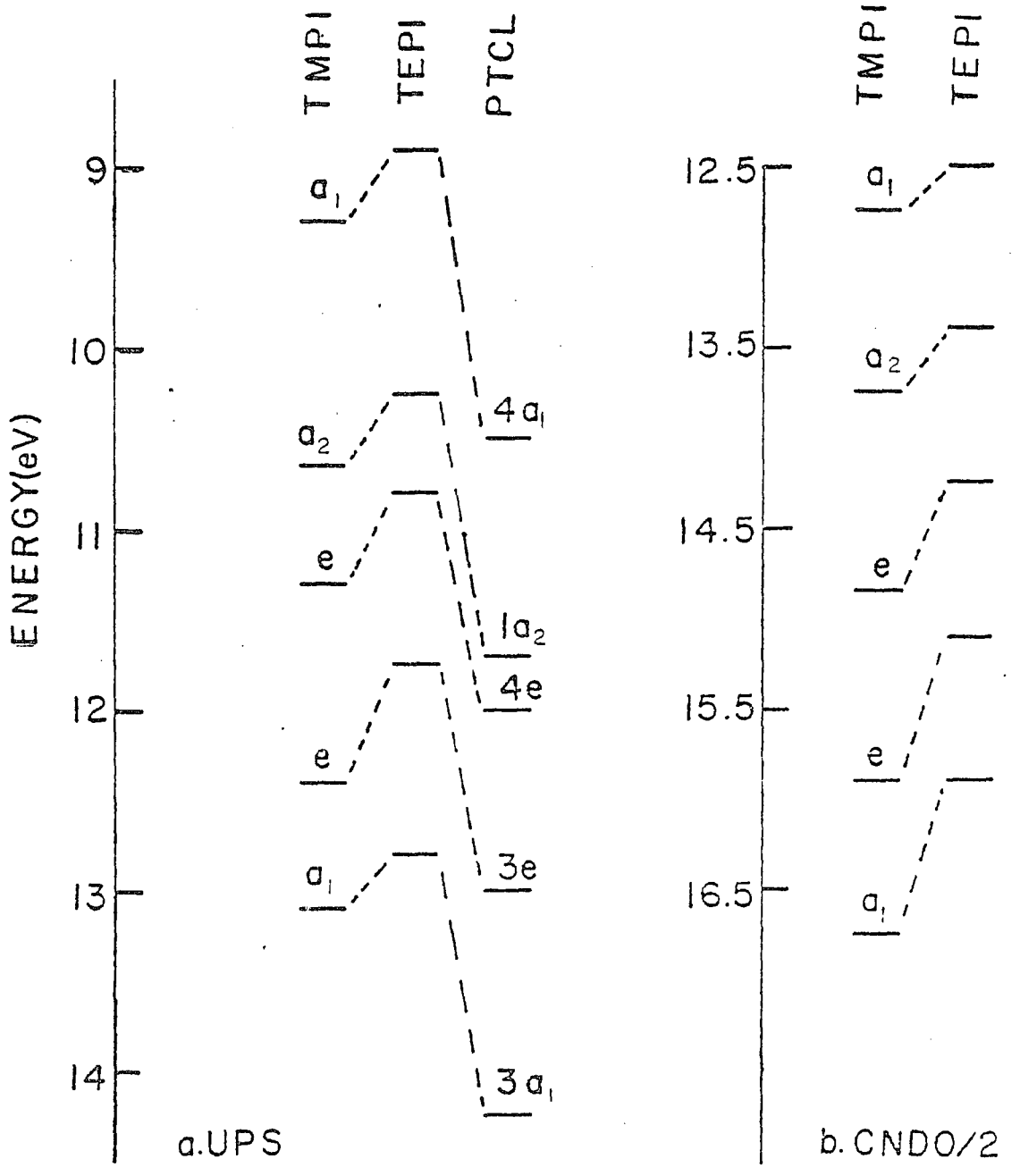
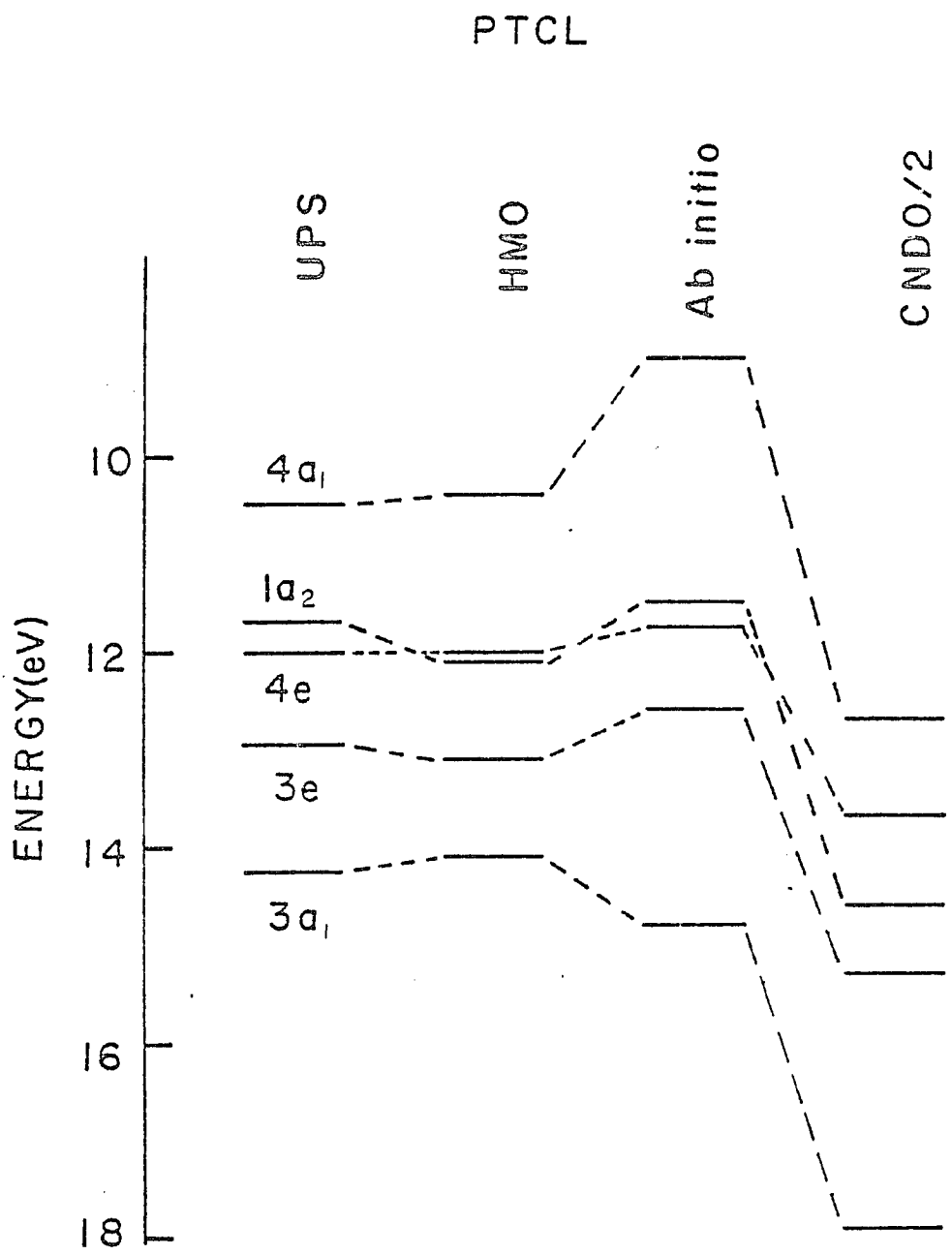

TMPI
TEPI
PTCL
ENERGY(eV)
9
10
11
12
13
14
a1
a2
e
e
a1
4a1
1a2
4e
3e
3a1
a.UPS
TMPI
TEPI
12.5
13.5
14.5
15.5
16.5
a1
a2
e
e
a1
b.CNDO/2

Figure 3. UPS, HMO, ab initio and CNDO/2 correlation diagram for PTCL.


PTCL
UPS
HMO
Ab initio
CNDO/2
ENERGY(eV)
10
12
14
16
18
4a1
1a2
4e
3e
3a1

five bands. Inspection of the UPS of TMPI. TEPI and PTCL suggests the following:

(i) The low-energy regions (9-15eV) of the UPS of TMPI and TEPI resembel that of PTCL.

(ii) The los-energy (9-15eV) ionization events of the phosphites are of lower energy than those of PTCL. This energy decrement reflects the order of atomic energy levels: Cl 3p is more tightly bound than O 2p.

(iii) The first five UPS bands of TMPI, contained in the 9-15eV region, lie at higher energies (~0.4eV) than their correspondents in TEPI. The fifth band of TEPI has been subsumed in the broad composite band at 12.85eV, which contains a variety of unidentified ionization events (such as C-C and C-H σ ionization events).

(iv) The first UPS band of the phosphites is relatively sharp and isolated. Since the HOMO of these compounds is expected to involve the P-lone pair on the phosphorus atom, as evidenced by studies on both phosphites[48] and phosphorus trichloride,[39a,39b,39c,40,47] this first UPS band undoubtedly represents the ionization event associated with the P-lone pair.

The low energy region should also contain ionization events associated with the O-lone pair (a and e type MO's) and the P-O ionization events. Finally, a comparison of the UPS correlation diagram for these molecules provides a significant vindication of the assignments of the phosphites. Thus, with these information on hand, the UPS analysis proceeds rather smoothly.

In TMPI, I(1), at 9.30eV involves ionization from an a_1 MO which is characterized by a large contribution from the P-lone pair on phosphorus. However, it should be noted that the reduced sharpness of

this band indicates that the P-lone pair is somewhat delocalized over the rest of the molecule. This contention is supported by the CNDO/2 computation which reveals a 66% contribution by the P 3p orbital to this a_1 MO. This MO correlates with the $4a_1$ MO of PTCL. This assignment of I(1) of TMPI agrees well with that made by Bettridge, et al.[48] Thus, the second and third ionization events probably are associated with the O-lone pairs. The second ionization event, I(2) = 10.63eV, represents ionization from an a_2 MO which is predominantly O 2p in character and non-bonding in nature (compare PTCL). This a_2 MO correlates with the $1a_2$ MO of PTCL. However, Bettridge, et al.[48] have assigned I(2) to ionization from an e MO which involves the O-lone pairs on the basis of relative peak areas (the validity of which is questionable). The assignment of I(2) as $I(a_2)$ is also supported by CNDO/2 computational results. After assigning I(2) as $I(a_2)$, it seems logical that I(3) = 11.29eV, should be assigned as I(e), which is largely O 2p in character and non-bonding in nature (compare PTCL). This e MO correlates with the 4e MO of PTCL. This assignment is also consistent with CNDO/2 computational results. However, Bettridge, et al.[48] have assigned I(3) to ionization from O-lone pair (a_2 type MO), and C-O (a and e type MO's) solely on the basis of relative band area considerations. The assignment of I(2) as $I(a_2)$ and I(3) as I(e) is further substantiated by CNDO/2 computational results which indicate a contribution of 78% and 57% by the O 2p orbital towards the a_2 and e type MO's respectively. Thus, the remaining two bands of the low-energy region, namely the 4th and 5th bands should involve ionization from bonding MO's. The fourth ionization event, I(4) = 12.42eV, is assigned as I(e), where this e type MO is strongly bonding in nature (compare PTCL).

This assignment agrees well with that made by Bettridge, et al.[48] and with CNDO/2 computationsl results. This e-type MO correlates with the 3e MO of PTCL. The fifth ionization event, I(5) = 14.23eV is assigned as $I(a_1)$, where this a_1 MO is P-O bonding in nature. This a_1-type MO correlates with the $3a_1$ MO of PTCL. This assignment is in agreement with that made by Bettridge, et al.[48] The CNDO/2 computational results also support this assignment.

The UPS of TEPI is assigned in a straightforward manner by comparison with those of TEPI and PTCL. These assignments are listed in Table 1. The CNDO/2 computational results also support these assignments. The shift in ionization events towards lower energy in going from TMPI to TEPI is in agreement with CNDO/2 computational results with indicate a reduced magnitude of the percentile O character in the MO's of TEPI relative to the corresponding set in TMPI.

The spacing between the experimental ionization energies agrees well with the energy gap between the CNDO/2 MO's for TMPI and TEPI as indicated in Figure 2. Lastly, the relative destabilization of MO's of TEPI compared to those of TMPI (by $\sim$ 0.4eV) is mimicked by the CNDO/2 results, the only exception being the a_1 type MO (which correlates with the $3a_1$ MO of PTCL) representing I(5). The experimental value of this shift of I(5) in going from TEPI to TMPI is $\sim$ 0.37eV whereas the CNDO/2 shift is $\sim$ 0.86eV. However, this discrepancy may be due to the imprecise location of I(5) which is imbedded in a rather broad composite band. Also, Estended Huckel computation reproduces the order of MO's represented by experimental ionization events.[53]

B. Phosphates. The UPS of TMPA and TEPA are displayed in Figure 4. Ionization events and their assignments are tabulated in Table 2. Since

Figure 4. UPS of TMPA and TEPA

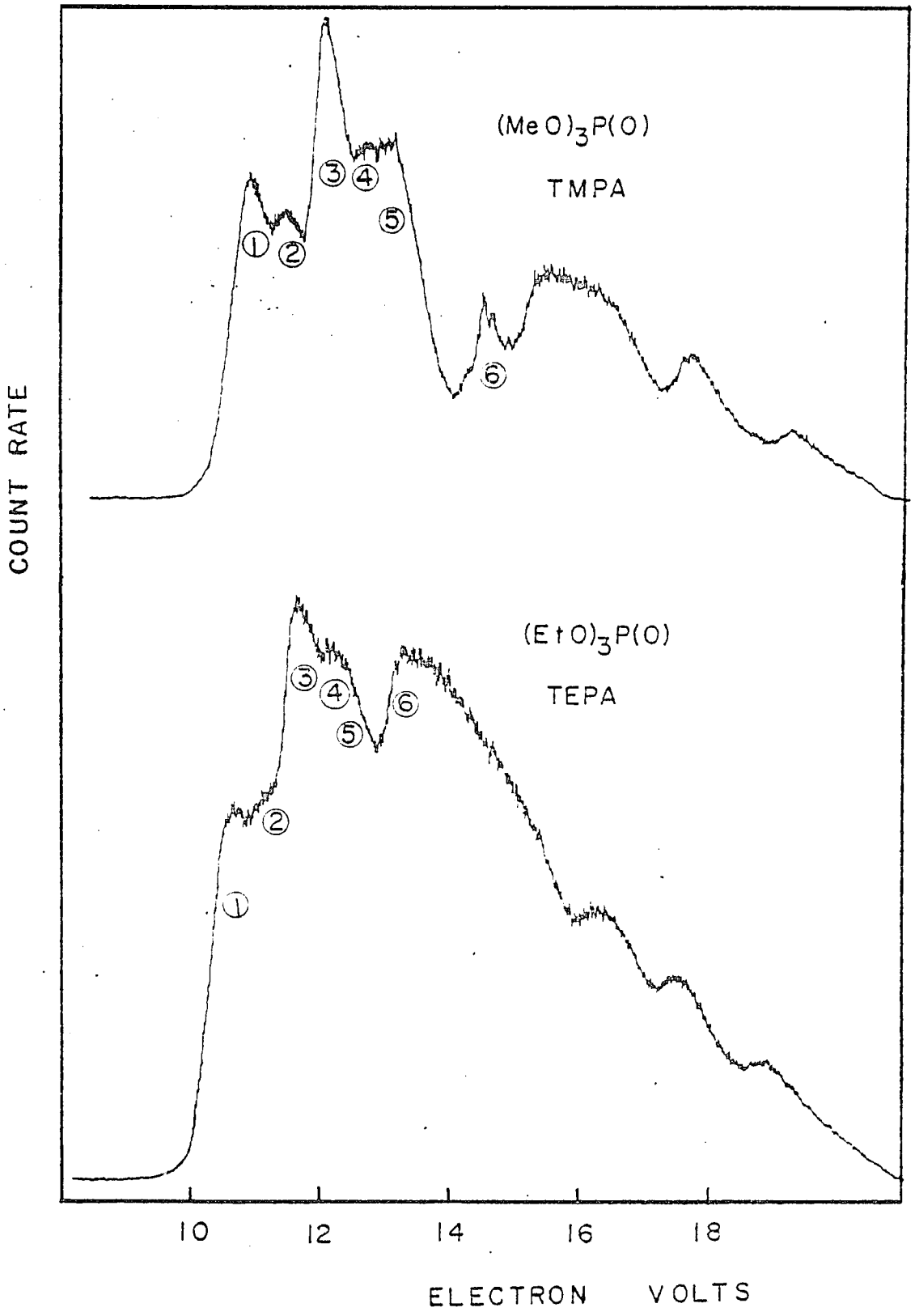

(MeO)3P(O)
TMPA
(EtO)3P(O)
TEPA
COUNT RATE
10
12
14
16
18
ELECTRON VOLTS

TABLE 2

UPS DATA (in eV) AND ASSIGNMENTS FOR POTCL, TMPA AND TEPA

Number Index	Compound	I(1)	I(2)	I(3)	I(4)	I(5)	I(6)
1.	POTCL[a]	11.89	12.36	12.97	13.46	13.85	15.36
	MO type Symmetry Designation[b]	O(Axial) Non-bonding 5e	Cl(Equatorial) Non-bonding $1a_2$	Cl(Equatorial) Non-bonding 4e	P-O(Axial) Bonding $5a_1$	Strongly Bonding 3e	P-Cl(Equatorial) Bonding $4a_1$
2.	TMPA	10.9	11.45	12.05	12.70	13.00	14.49[c]
	MO type Symmetry Designation	O(Equatorial) Non-bonding a_2	O(Axial) Non-bonding e	O(Equatorial) Non-bonding e	P-O(Axial) Bonding a_1	Strongly Bonding e	P-O(Equatorial) Bonding a_1
3.	TEPA	10.69	11.10	11.66	12.12	12.40[d]	13.26[d]
	MO type Symmetry Designation	O(Equatorial) Non-bonding a_2	O(Axial) Non-bonding e	O(Equatorial) Non-bonding e	P-O(Axial) Bonding a_1	Strongly Bonding e	P-O(Equatorial) Bonding a_1

a. Taken from Ref.[40,47,48]

b. The outer valence electronic configuration is identical to that of Ref. 9.

c. Displays vibrational fine structure with a spacing of $\sim 1000\ cm^{-1}$.

d. Part of a broad composite band.

these molecules can be categorized in the C_{3v} point group, their MO's are labelled a_1, a_2, and e. Moreover, this set of MO's correlates with the corresponding set of MO's for phosphorus oxytrichloride (POTCL). The UPS correlation diagram for TMPA, TEPA and POTCL is displayed in Figure 5. Figure 5 also constitutes the CNDO/2 correlation diagram for TMPA and TEPA. Since the CNDO/2 method[40] fails to reproduce the UPS order of MO's for POTCL, CNDO/2 computations for POTCL were not included in Figure 6. However, for completeness, UPS,[39a,40,46,47,48] CNDO/2,[40] HMO[40] and ab initio[44,45] correlation diagram for POTCL is presented in Figure 6. A close examination of Figure 6 deserves the following comments:

(i) Ab initio computations reproduce the MO order as deduced from UPS. However, it underestimates the first five ionization events in POTCL.

(ii) The CNDO/2 computation predicts that the $5a_1$ MO is the HOMO in POTCL, whereas, it has been inferred from UPS measurements that $5a_1$ is actually 4th lowest in the sequence of filled MO's. Moreover, it overestimates the ionization energies.

(iii) The HMO method reproduces the experimental MO sequence. But it fails to reproduce the energy gaps between the various ionization events.

The accepted MO order in POTCL is $5e > 1a_2 > 4e > 5a_1 > 3e > 4a_1$. The nature and characteristics of these MO's are outlined in Table 2.

An inspection of the UPS of TMPA, TEPA and phosphites leads to the following comments:

(i) The low-energy UPS region (9-15eV) of TMPA contains six

Figure 5. The UPS correlation diagram for POTCL, TMPA and TEPAE and a CNDO/2 CORRELATION DIAGRAM FOR TMPA and TEPA.

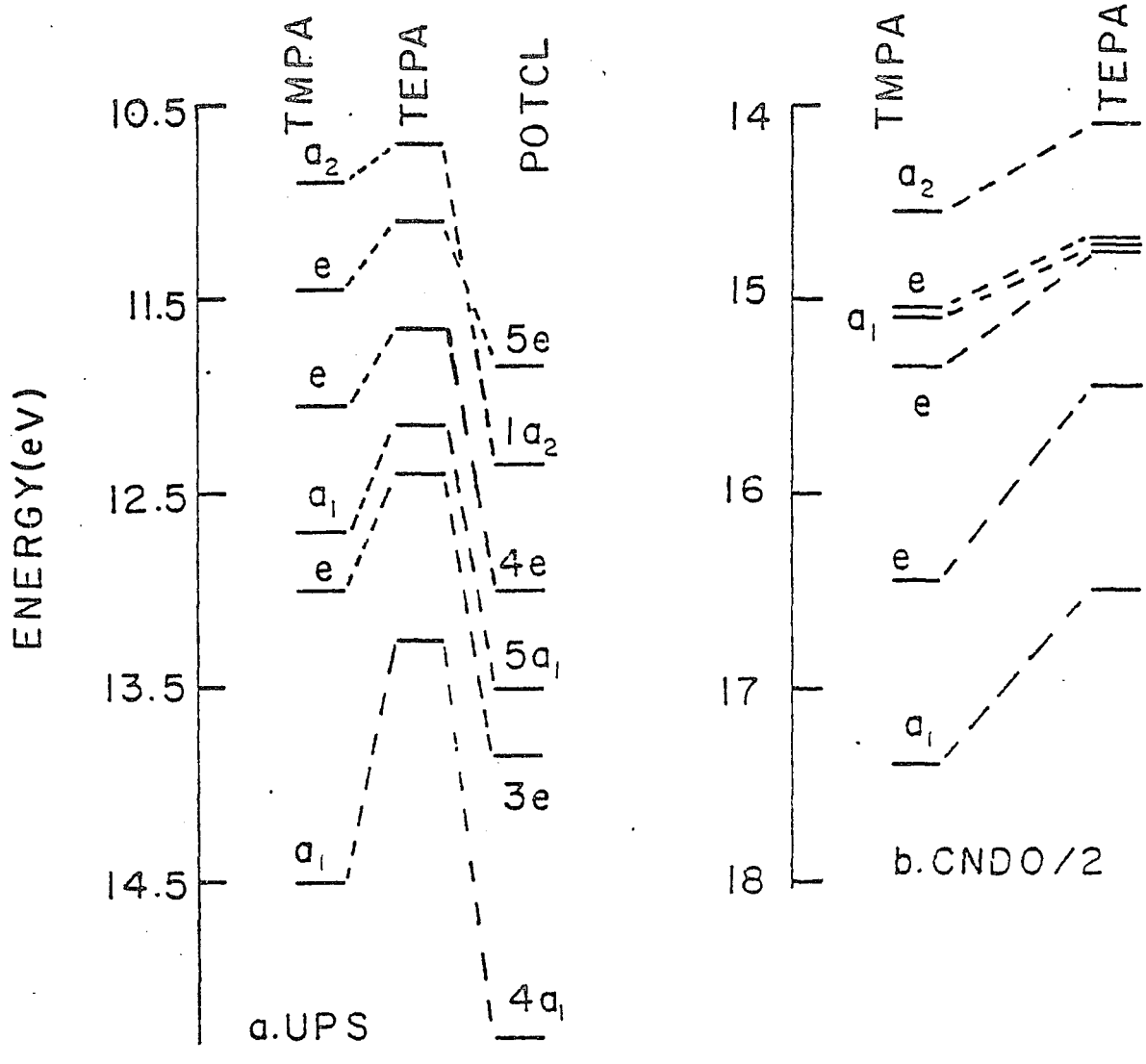
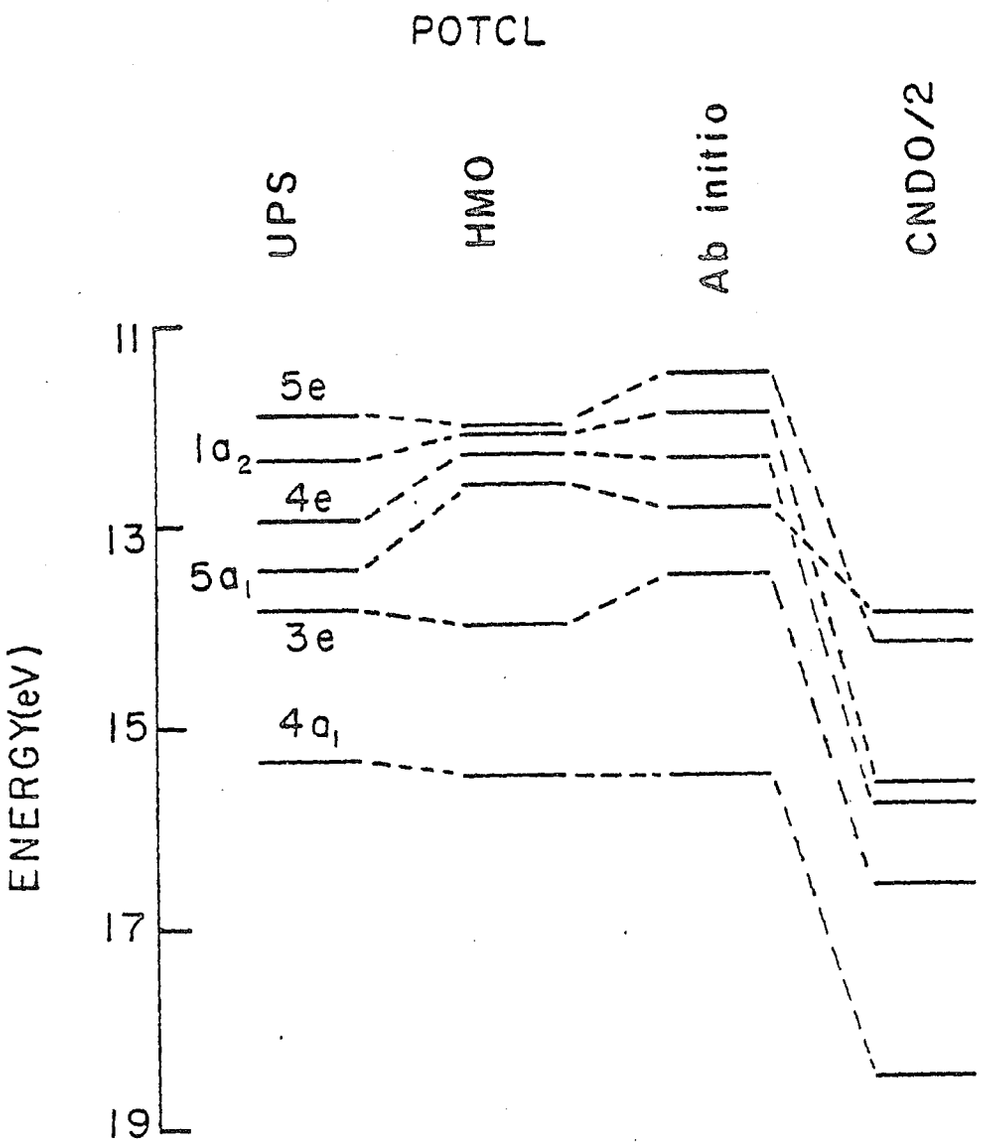

ENERGY(eV)
10.5
11.5
12.5
13.5
14.5
TMPA
TEPA
POTCL
a2
e
e
a1
e
a1
5e
1a2
4e
5a1
3e
4a1
a.UPS
14
15
16
17
18
TMPA
TEPA
a2
a1
e
e
e
a1
b.CNDO/2

Figure 6. UPS, HMO, ab initio and CNDO/2 correlation diagram for POTCL


POTCL
UPS
HMO
Ab initio
CNDO/2
ENERGY(eV)
11
13
15
17
19
5e
1a2
4e
5a1
3e
4a1

bands. Although the same observation is made with regard to POTCL, it appears that the band shapes of POTCL differ significantly from those of TMPA. Moreover, the ionization events of TMPA are shifted by ~ 1eV towards lower energy relative to those of POTCL. This destabilization of the MO's of TMPA relative to those of POTCL is due to the fact that energetically O 2p AO > Cl 2p AO.

(ii) The UPS of TEPA resembles that of TMPA with the exception that the 4th and 5th bands of TEPA have coalesced and that the 6th band has become part of a broad composite band which contains other unidentified C-C and C-H σ ionization events. Also, the ionization events of TEPA occur at lower energies than those of TMPA.

(iii) Although the UPS of the phosphates are very similar to those of phosphites, the following differences in the gross features of the phosphates are obvious:

(a) The phosphate spectra do not exhibit P-lone pair band.

(b) An O (Axial) non-bonding ionization event occurs in the spectra of phosphates but not in those of the phosphites.

(c) An ionization event associated with the P-O (Axial) bonding MO, the formation of which is facilitated by electron donation from the top-most filled a_1 (σ) MO of the phosphites, is present in the phosphates. Thus, although this ionization event is absent in phosphite, it must correlate with the lowest-energy ionization event, namely the a_1, P-lone pair ionization event, of the phosphites.

The ionization events of phosphates shift towards higher energies relative to the phosphites. This stabilization of the phosphate MO's relative to the corresponding set of phosphite MO's is due to the introduction of the electronegative oxygen atom.[48] A comparison of the

UPS of POTCL and PTCL reveals the same effect.

(iv) A comparison of the band shapes of the first two UPS bands of TMPA and POTCL indicates that the order of the two topmost MO's of POTCL might well have inverted in TMPA. In POTCL, the $1a_2$ MO consists solely of Cl 3p orbitals (100% contribution), whereas the Cl3p orbitals contribute only 55% towards the 5e MO.[47] Consequently one may expect a reversal of the ordering of the 5e and $1a_2$ MO's of POTCL relatively to that of TMPA simply on the basis of energetic consideration of O 2p and Cl 3p atomic orbitals. With these suppositions in mind, an attempt can be made to analyze the UPS of phosphates.

In TMPA, I(1) = 10.9eV represents ionization from an a_2 type MO which relates to the $1a_2$ MO of POTCL. It should be noted that this band is sharp and well-defined, indicating ionization from a non-bonding MO. This a_2 MO is stabilized by $\sim$ 0.3eV relative to the corresponding a_2 MO in the phosphites. The second ionization event, I(2) = 11.45eV, is assigned as I(e), where the e MO has a large contribution from O (axial) 2p atomic orbital and is non-bonding in nature. This e MO correlates with the 5e MO of POTCL. This ionization event is absent in the phosphites. However, Bettridge, et al.[48] have assigned I(1) as I(e) despite the fact that comparison of the shapes of the first two bands of TMPA and POTCL indicates that the assignment of I(2) as I(e) is more likely than the alternative assignment of Bettridge, et al.[48] namely I(1) as I(e). Moreover, this particular order of MO's: a_2 (which corresponds to $1a_2$ MO of POTCL) > e (which corresponds to 5e MO of POTCL), is expected on the basis of MO compositions as derived from CNDO/2 computations. In the structurally-related compound, H_3PO_4, the CNDO/2[53] computational results predict $1a_2$ to be the

The third ionization event, I(3) = 12.05eV is assigned as I(e), where this e MO corresponds to the 4e MO of POTCL. Moreover, this e MO is stabilized by ~ 0.7eV relative to its correspondent e MO in TMPI (compare POTCL and PTCL). The fourth ionization event, I(4) = 12.7eV, is assigned as $I(a_1)$ where this a_1 MO, which is the counterpart of the $5a_1$ MO of POTCL, is P-O (Axial) bonding in nature. Consequently, this a_1 type MO is related to the a_1 HOMO of phosphites. This depression of the a_1 HOMO of phosphites by ~ 3.4eV on formation of P-O (Axial) bond is in excellent agreement with similar effects in PF_3/POF_3 and $PCl_3/POCL_3$ pairs. The fifth ionization event, I(5) = 13.0eV is assigned as I(e), where this e MO is the counterpart of the 3e MO of POTCL. This e MO, which is strongly bonding in nature, is destabilized by ~ 0.85eV relative to the 3e MO of POTCL. Moreover, this e MO is stabilized by ~ 0.6eV relative to the corresponding e MO in TMPI (compare POTCL and PTCL). The sixth ionization event, I(6) = 14.49eV, is assigned as $I(a_1)$, where this a_1 MO, which is the counterpart of the $4a_1$ MO in POTCL, is P-O (Equatorial) bonding in nature and is destabilized by ~ 0.9eV relative to the $4a_1$ MO in POTCL. This ionization event exhibits vibrational excitation. The observed spacing of ~ 1000 cm^{-1}, which is in close agreement with the P-O stretching frequency of 1050 cm^{-1} in the neutral molecule,[54] suggests that the symmetrical P-O stretching mode is excited. Ionization from the $4a_1$ MO of $POCL_3$ and POF_3 also involves similar vibrational excitation.[47] Finally, this a_1 MO is stabilized by ~ 1.3eV relative to the corresponding a_1 MO in TMPI (compare POTCL and PTCL).

The CNDO/2 computational results reproduce the above ordering of UPS MO's with the single exception of the first a_1 MO which corresponds

to $5a_1$ MO in POTCL. This anomaly is also observed with POTCL[40]. Thus, it may well be an oddity of the CNDO/2 computation.

The UPS of TEPA is analyzed in a straightforward manner by comparing it with that of TMPA. The assignments are tabulated in Table 2. The destabilization of the MO's of TEPA relative to TMPA agrees well with the magnitude of destabilization of the MO's of TEPI relative to those of TMPI. Furthermore, the MO stabilizations relative to TEPI compare favourably with the stabilization magnitudes of TMPI relative to those of TMPA. The CNDO/2 results for TEPA mimic the ordering of MO's as deduced from UPS, with the single exception of the first a_1 MO which is misplaced. The same observation pertains to POTCL and TMPA.

C. P-O (Axial) Bonds in Phosphates. The ligand properties of phosphites can be described in terms of their σ-doner and π-acceptor capabilities. In going from phosphite to phosphates, bonding occurs through electron donation from the highest-filled MO of symmetry $a_1(\sigma)$, which is predominantly localized on the phosphorus atom, and by electron acceptance into the first virtual orbital of symmetry $e(\pi)$, which has substantial phosphorus 3d character.[55] Table 3 displays the results of CNDO/2 calculations relevant to the present discussion. On formation of phosphates from phosphites, there is a net donation of 0.24e from phosphorus to oxygen atom. This process is accompanied by a reduction in the phosphorus 3s and $3p\sigma$ AO populations and an increase in the $3p\pi$ and $3d\pi$ AO populations. This effect is a direct consequence of the donor-acceptor properties of phosphites.

In phosphites, the HOMO, which is of a_1 symmetry and has the predominent characteristics of the P-lone pair orbital, has $\sim$ 32% P 3s AO character, while the corresponding MO (which correlates with the

TABLE 3

AO POPULATIONS OF PHOSPHITES

AND PHOSPHATES

Phosphorus AO	TMPI	TMPA	TEPI	TEPA
3s	1.72	1.00	1.72	1.03
3p(a_1)	0.79	0.61	0.80	0.61
3p(e)	0.88	1.09	0.88	1.09
3d(a_1)	0.25	0.32	0.25	0.32
3d(e)	1.02	1.40	1.02	1.39
Atomic Charge	0.33	0.57	0.31	0.56

$5a_1$ MO in POTCL) in phosphates has ~ 1% P 3s AO character. The major component of the latter MO is the O 2p AO (~ 70%). This delocalization explains the increase (~ 3.4eV) of the ionization energy caused by coordination. The first e MO of phosphates (ie., the MO which corresponds to the 5e MO of POTCL), which is the acceptor orbital of POTCL, has 7% and 3% P 3d character in TMPA and TEPA, respectively, accounting for much of the increase in P 3d population on coordination. All these results compare favourably with the results of ab initio computations for PF_3 and POF_3.[55]

A close examination of Table 3 reveals the following changes in orbital populations between the phosphates and phosphites.

(i) Populations of P 3s and P 3pσ orbitals decrease by ~ 0.7e and ~ 0.2e, respectively.

(ii) Populations of P 3pπ and P 3dπ orbitals increase by ~ 0.2e and ~ 0.4e, respectively.

(iii) There is an increase in formal charge on the P atom by ~ +0.24, while the charges on other atoms are affected but little.

D. Substituted Phosphates. The UPS of DEDTPA, DECLTPA, DECLPA and DMMPNA are displayed in Figure 7. Ionization events and their assignments are tabulated in Table 4. Since this set of molecules can be categorized in the C_s point group, their MO's are labelled a' and a''. The UPS correlation diagram for POTCL, DEDTPA, DECLTPA, DECLPA and DMMPNA is presented in Figure 8. Figure 8 also contains a CNDO/2 correlation for DEDTPA, DECLTPA, DECLPA and DMMPNA. The labels in the CNDO/2 correlation diagram refer to the MO's in POTCL from which the MO's of these compounds derive. The MO's which are degenerate in phosphates and phosphites (C_{3v} point group) will be split into a' and a'' MO's in substituted

Figure 7. UPS of DEDTPA, DECLTPA, DECLPA and DMMPNA

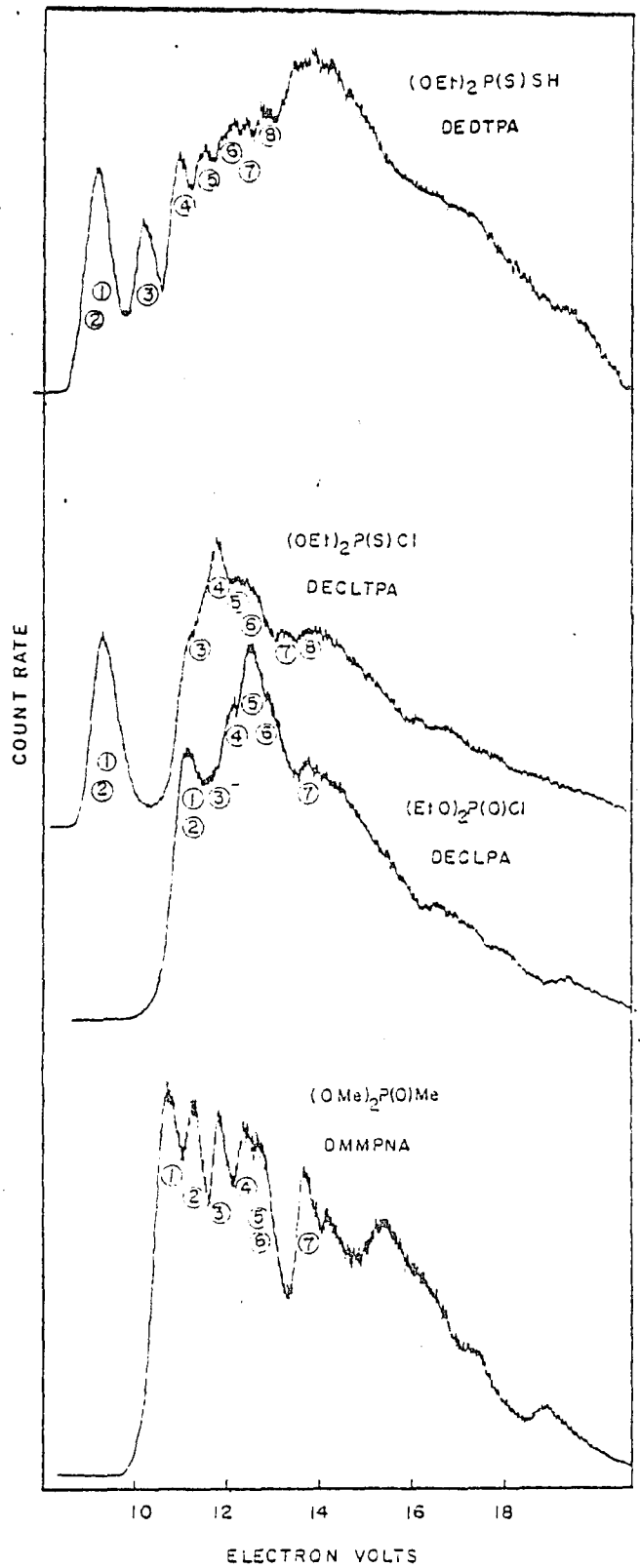

(OEt)2P(S)SH
DEDTPA
(OEt)2P(S)Cl
DECLTPA
(EtO)2P(O)Cl
DECLPA
(OMe)2P(O)Me
DMMPNA
COUNT RATE
10
12
14
16
18
ELECTRON VOLTS

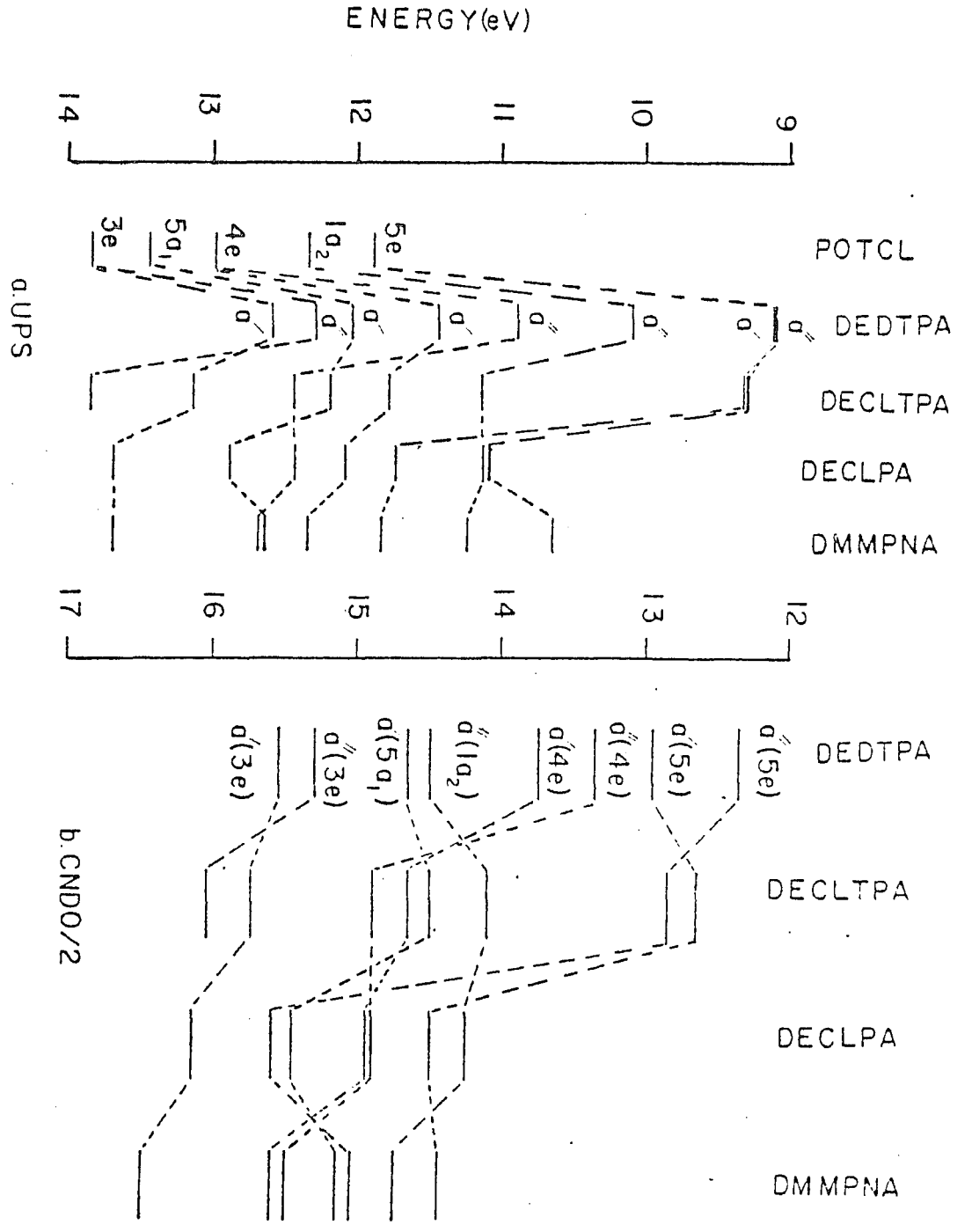
TABLE 4

UPS DATA (in eV) AND ASSIGNMENTS FOR

DEDTPA, DECLTPA, DECLPA and DMMPNA

Number Index	Compound	I(1)	I(2)	I(3)	I(4)	I(5)	I(6)	I(7)	I(8)
1.	DEDTPA	9.14	9.14	10.12	10.89	11.42	12.03	12.29	12.60
	Symmetry designation of the MO involved	a''	a'	a''	a''	a'	a'	a''	a'
	Parentage with POTCL as reference	5e	5e	$1a_2$	4e	4e	$5a_1$	3e	3e
2.	DECLTPAE	9.31	9.31	11.10	11.80	12.20	12.46	13.20	13.84
	Symmetry designation of the MO involved	a'	a''	a''	a'	a'	a''	a'	a''
	Parentage with POTCL as reference	5e	5e	$1a_2$	4e	$5a_1$	4e	3e	3e
3.	DECLPAE	11.07	11.07	11.74	12.09	12.46	12.90	13.70	
	Symmetry designation of the MO involved	a'	a''	a''	a'	a''	a'	a'	
	Parentage with POTCL as reference	5e	$1a_2$	5e	4e	4e	$5a_1$	3e	
4.	DMMPNAE	10.71	11.26	11.83	12.37	12.65	12.65	13.68	
	Symmetry designation of the MO involved	a'	a''	a''	a'	a''	a''	a'	
	Parentage with POTCL as reference	5e	$1a_2$	5e	4e	4e	$5a_1$	3e	

Figure 8. UPS correlation diagram for POTCL, DEDTPAE, DECLTPA, DECLPA and DMMPNA. It also contains a CNDO/2 correlation diagram for DEDTPA, DECLTPA, DECLPA and DMMPNA.


ENERGY(eV)
14
13
12
11
10
9
a.UPS
3e
5a1
4e
1a2
5e
POTCL
DEDTPA
DECLTPA
DECLPA
DMMPNA
17
16
15
14
13
12
b.CNDO/2
a'(3e)
a''(3e)
a'(5a1)
a''(1a2)
a'(4e)
a''(4e)
a'(5e)
a''(5e)
DEDTPA
DECLTPA
DECLPA
DMMPNA

phosphates (C_s point group). Moreover, there is the possibility that the MO's of the same symmetry will mix with one another.

A close examination of the UPS of DEDTPA, DECLTPA, DECLPA, DMMPNA and TEPA suggests the following:

(i) The UPS of DECLPA is very similar to that of TEPA. The ionization events of DECLPA have shifted to higher energy relative to those of TEPA.

(ii) In DECLTPA and DEDTPA, the first two bands are rather sharp and isolated. Thus, this band may involve ionization from the non-bonding P-S (Axial) MO.

(ii) In DEDTPA, the second band, at 10.12eV, which is but about half as intense as the first bond, may well be associated with an S-lone pair ionization from the -SH group since this band is absent in DECLTPA.

(iv) The ionization events of DEDTPA occur at lower energy than those of DECLTPA.

The comparison of the UPS of these compounds with those of TMPA, POTCL and $SPCl_3$ provides a valuable tool for analyzing their spectra.

In DEDTPA and DECLTPA the first band, which occurs at 9.14 and 9.31 eV, is sharp and has the same band shape. Hence, it must contain ionization events associated with a' and a'' MO's which are related to the 5e MO's of POTCL and $SPCl_3$. The S(Axial) lone pair makes a rather large contribution towards these a' and a'' MO's. These a' and a'' MO's of DEDTPA and DECLTPA are destabilized by 2.0eV relative to the corresponding MO's of POTCL. This is hardly surprizing since these MO's have $\sim$ 60% S character. Also, the width of this first band in DEDTPA and DECLTPA is large enough to contain two ionization events. CNDO/2 computation also supports this contention. Also, this assignment compares favourably with

the S-lone pair ionization in thioformaldehyde which occurs at 9.38eV.[56]

In DEDTPA, the second band at 10.12eV is half as intense as the first band and is absent in DECLTPA. Thus, simply from the point of view of naive intensity arguments, the second band must contain the S-lone pair ionization of the -SH group. Thus, I(3) = 10.12eV, is assigned as I(a''), where this a'' MO is related to the $1a_2$ MO of POTCL. This assignment, compares favourably with the S-lone pair ionization of the -SH group in CH_3-SH at 9.44eV.[57] In DEDTPA, I(4) = 10.89eV and I(5) = 11.42eV, are tentatively assigned as I(a'') and I(a') where these a'' and a' MO's relate to the 43 MO of POTCL and TEPA. The assignment I(5) as I(a'') agrees favourably with I(5) of TEPA (i.e., the ionization event from the O(Equatorial) lone pair which relates to the 4e MO of POTCL), which occurs at 11.66eV. The sixth ionization event in DEPTA, I(6) = 12.03eV, is assigned tentatively as I(a') where this a' MO corresponds to the $5a_1$ MO in POTCL and $SPCL_3$. This assignment agrees with that of I($5a_1$) in $SPCl_3$ and TEPA (which occurs at 12.65 and 12.12eV, respectively). In DEDTPA, I(7) = 12.29eV and I(8) = 12.60eV, are assigned tentatively as I(a'') and I(a'), where these a'' and a' MO's are related to the 3e MO of POTCL and TEPA. This assignment agrees well with I(3e) = 12.40eV in TEPA.

In DECLTPA, I(1) = 9.31eV and I(2) = 9.31eV are assigned as I(a') and I(a'') on the basis of comparison of the first two bands of DECLTPA and DEDTPA. These a' and a'' MO's are related to the 5e MO in POTCL. The third ionization event, I(3) = 11.10eV, is tentatively assigned as I(a''), where this a'' MO corresponds to $1a_2$ MO in POTCL. This assignment agrees favourably with I($1a_2$) = 10.69eV in TEPA. The fourth ionization event, I(4) = 11.80eV, is tentatively assigned as I(a'),

where this a' MO corresponds to 4e MO in POTCL. This assignment agrees well with I(4e) = 11.66eV in TEPA. The fifth ionization event, I(5) = 12.20eV, is assigned tentatively as I(a') where this a' MO corresponds to $5a_1$ MO in POTCL. This assignment is consistent with I($5a_1$) in TEPA and DEDTPA (which occur at 12.12eV and 12.03eV, respectively). Also, in this compound, I(6) = 12.46eV is assigned tentatively as I(a''), where this a'' MO derives from the 4e MO in POTCL and $SPCl_3$. This assignment is in favourable agreement with I(4e) = 12.65eV in $SPCl_3$. In DECLTPA, I97) = 13.20eV and I(8) = 13.84eV, are tentatively assigned as I(a') and I(a''), respectively, where these a' and a'' MO's correspond to the 3e MO of POTCL. These assignments are consistent with I(3e)= 13.39eV in $SPCl_3$.

In DECLPAE, I(1) = 11.09eV is tentatively assigned as I(a'), where this a' MO is derived from 5e MO in POTCL. This assignment compares favourably with I(5e) = 11.10eV in TEPA. The second ionization event, I(2) = 11.10eV, is tentatively assigned as I(a''), where this a'' MO derives from the $1a_2$ MO in POTCL. This assignment is consistent with I($1a_2$) = 10.69eV and I($1a_2$) = 11.20eV in TEPA and DECLTPA, respectively. The third ionization event, I(3) = 11.74eV, which measures well with I(5e) = 11.89eV in POTCL, is assigned tentatively as I(a'') where this a'' MO is related to 5e MO in POTCL. In this compound, I(4) = 12.09eV and I(5) = 12.46eV, are assigned tentatively as I(a') and I(a'') where these a' and a'' MO's correspond to 4e MO in POTCL. These assignments match the corresponding set of assignments in DECLTPA. The sixth ionization event, I(6) = 12.90eV is tentatively assigned as I(a'), where this a' MO is derived from $5a_1$ MO in POTCL. This assignment is consistent with I($5a_1$) = 12.20eV in DECLTPA. Also, this assignment agrees well with

$I(5a_1)$ = 13.46eV in POTCL. The seventh ionization event, I(7) = 13.70 eV is tentatively assigned as I(a'), where this a' MO is related to 3e MO in POTCL. This assignment matches well with I(7e) = 13.84eV in POTCL.

In DMMPNA, I(1) = 10.71eV is tentatively assigned as I(a'), where this a' MO is related to 5e MO in POTCL. The second ionization event, I(2) = 11.26eV, is assigned tentatively as I(a'), where this a' MO is derived from $1a_2$ MO in POTCL. The third ionization event, I(3) = 11.83 eV, is assigned tentatively as I(a''), where this a'' MO corresponds to 5e MO in POTCL. This assignment agrees well with the assignment of I(3) as I(a'') in DECLPAE (I(3) = 11.74eV), where this a'' MO corresponds to 5e MO in POTCL. In this compound, I(4) = 12.37eV is assigned tentatively as I(a') where this a' MO is derived from 4e MO in POTCL. The fifth ionization event, I(5) = 12.65eV, is assigned as I(a'), where this a' MO corresponds to $5a_1$ MO in POTCL. This assignment compares favourably with $I(5a_1)$ = 12.70eV in TMPA The sixth ionization event, I(6) = 12.65eV, is tentatively assigned as I(a''), where this a'' MO is related to 4e MO in POTCL. The seventh ionization event, I(7) = 13.60eV is assigned as I(a') where this a' MO corresponds to 3e MO in POTCL. This assignment is in agreement with the corresponding assignment of I(7) as I(a') in DECLPA.

The CNDO/2 computational results presented in figure 8 reproduce the ordering of MO's as observed in UPS with a few exceptions. In DEDTPA, the a'' MO which is derived from $1a_2$ MO in POTCL is misplaced. In DECLTPA and DMMPNA, the a' MO which corresponds to $5a_1$ MO in POTCL is misplaced. However, the failure to predict the correct location of $5a_1$ MO may be an oddity of the CNDO/2 method.[40] In DECLPA, the a'' MO,

which is derived from the 5e MO of POTCL is misplaced.

III. CONCLUSIONS

This work summarizes and analyzes the UPS results of phosphites, phosphates and substituted phosphates. The salient features of this work are:

(1) Assignment of the UPS of phosphites, phosphates, and substituted phosphates have been made.

(2) The change of spectral features of phosphites relative to those of phosphates has been explained using the σ-donation and π-acceptance properties of phosphites.

(3) The effects of substitution as well as symmetry lowering have been utilized to explain the change in spectral features of phosphates relative to those of substituted phosphates.

CHAPTER IV

REFERENCES

REFERENCES

1. D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970.
2. A. B. F. Duncan, "Rydberg Series in Atoms and Molecules", Academic Press, New York and London, 1971.
3. T. Koopmans, Physica, 1, 104 (1934).
4. W. J. Rabalais, "Principles of Ultraviolet Photoelectron Spectroscopy", Wiley-Interscience, New York, 1976.
5. W. J. Richard, Int. J. Mass. Spectrom. Ion. Phys., 2, 419 (1969).
6. M. B. Robin, F. A. Bovey and H. Basch, in "The Chemistry of Amides", (J. Zabicky, ed.), Chapter I, Interscience Publishers, New York, 1970.
7. P. Karlson, "Introduction to Modern Biochemistry", 2nd ed., Academic Press, New York, 1965.
8. R. Hoffmann, Accounts Chem. Res., 4, 1 (1971); E. Heilbronner, Israel J. Chem., 10, 143 (1972).
9. D. R. Dougherty, Ph.D. Dissertation, L.S.U. (Baton Rouge, LA. 70803), 1977.
10. QCPE: CNDO 141. See also, D. P. Santry and G. A. Segal, J. Chem. Phys., 47, 158 (1967). J. A. Pople and G. A. Segal, J. Chem. Phys., 43, S136 (1965).
11. QCPE: CNDO 174. See also, J. Del Bene and H. H. Jaffé, J. Chem. Phys., 48, 1807, 4050 (1968); 49, 1221 (1968).

12. D.O. Cowan, R. Gleiter, J. A. Hashmall, E. Heilbronner and V. Hornung, Angew. Chem. Internat. Edit. 10, 401 (1971).

13. J. R. Swenson and R. Hoffman, Helv. Chim. Acta, 53, 2331 (1970).

14. R. Hoffmann, Accounts Chem. Res., 4, 1 (1970).

15. T. K. Ha and W. Hug, Helv. Chim. Acta, 54, 2278 (1971).

16. A. Schweig, H. Vermeer and U. Weidner, Chem Phys. Letters, 26, 229 (1974).

17. M. Almemark, J. E. Backvall, C. Moberg, B. Akermark, L. Asbrink and B. Roos, Tetrahedron, 30, 2503 (1974).

18. J. L. Meeks, J. F. Arnett, D. Larson and S. P. McGlynn, Chem. Phys. Letters, 30, 2503 (1975).

19. K. N. Houk, L. P. Davis, G. R. Newkome, R. E. Duke and R. V. Nauman, J. Amer. Chem. Soc., 95, 8364 (1975).

20. J. L. Meeks, J. F. Arnett, D. Larson and S. P. McGlynn, J. Amer. Chem. Soc., 97, 3905 (1975).

21. S. P. McGlynn and J. L. Meeks, J. Electron Spectros. Relat. Phenom., 6, 269 (1975).

22. J. L. Meeks and S. P. McGlynn, J. Electron Spectros. Relat. Phenom., 8, 85 (1976).

23. J. L. Meeks and S. P. McGlynn, J. Amer. Chem. Soc., 97, 5079 (1975).

23. J. L. Meeks, H. J. Maria, P. Brint and S. P. McGlynn, Chem. Rev., 75, 603 (1975).

25. J. L. Meeks and S. P. McGlynn, Spectros. Letters, 8, 439 (1975).

26. D. Dougherty, J. J. Bloomfield, G. R. Newkome, J. F. Arnett and S. P. McGlynn, J. Phys. Chem., 80, 2212 (1976).

27. D. Dougherty, K. Wittel, J. Meeks and S. P. McGlynn, J. Amer. Chem. Soc., 98, 3815 (1976).

28. D. Dougherty and S. P. McGlynn, J. Amer. Chem. Soc., 100, 5597 (1978).

29. D. R. Dougherty, Ph.D. Dissertation, L.S.U. (Baton Rouge, LA 70803), 1977.

30. QCPE: CNDO 174. See also, J. Del Bene and H.H. Jaffe, J. Chem. Phys., 48, 1807, 4050 (1968); 49, 1221 (1968).

31. J. L. Meeks, Ph.D. Dissertation, L.S.U. (Baton Rouge, LA. 70803), 1974.

32. D. B. Larson, Ph.D. Dissertation, L.S.U. (Baton Rouge, LA 70803), 1972.

33. F. Fourneau and S. Sabetaz, Bull. Soc. Chim., 45, 834 (1929).

34. P. Dobosh, CNINDO: CNDO and INDO Molecular Orbital Program (Fortran IV), Program 141, QCPE., Indiana University, Bloomington, IN.

35. L. E. Sutton, "Tables of Interatomic Distances", Spec. Publ. No. 11, Chem. Soc. London, 1958; Supplement Spec. Publ. No. 18, (1965).

36. D. A. Sweigart and D. W. Turner, J. Amer. Chem. Soc., 94, 5592 (1972).

37. S. Chattopadhyay, unpublished results.

38. J. C. Bunzli, D. C. Frost and C. A. McDowell, J. Electron. Spectros. Relat. Phenom. 1, 481 (1972/73).

39. (a) P. J. Bassett and D. R. Lloyd, Dalton Trans., 3, 248 (1972).

(b) A. W. Potts, H. J. Lempka, D. G. Streets and W. C. Price, Philos. Trans. R. Soc. Lond. A 268, 59 (1970).

(c) P.J.Bassett, Ph.D. Thesis, University of Birmingham (1970).

40. P. A. Cox, S. Evans, A. F. Oxchard, N. V. Richardson and P. J. Roberts, Discussion Faraday Soc., 54, 26 (1972).

41. E. L. Wagner, J. Chem. Phys., 37, 751 (1963).

42. K. A. R. Mitchell, Can. J. Phys , 46 3499 (1968).

43. (a) I. H. Hillier and V. R. Saunders, Chem. Commun., 1183 (1970);

(b) I. H. Hillier and V. R. Saunders, Chem. Commun., 1510 (1970);

(c) I. H. Hillier and V. R. Saunders, J. Chem. Soc., (A), 664 (1970);

(d) I. H. Hillier and V. R. Saunders, J. Chem. Soc., (A), 2745 (1970);

(e) I. H. Hillier and V. R. Saunders, J. Chem. Soc. Dalton, 21 (1972);

(f) M. F. Guest, I. H. Hillier and V. R. Saunders, J. Chem. Soc. Faraday II, 867 (1972)

44. (a) A. Seravini and J. F. Labarre, Chem. Commun., 996 (1971);

(b) J. Demuynck and A. Veillard, Chem. Commun., 873 (1970);

(c) I. Absar and J. R. Van Wazer, J. Phys. Chem., 75, 1360 (1971);

(d) P. Castan, M. C. Labarre and J. F. Labarre, J. Chim. Phys., 66, 1908 (1969).

45. (a) L. S. Bartell, L. S. Su and Hsiukang Yow, Inorg. Chem., 9, 1903 (1970);

(b) H. Marsmann, L. C. D. Groenweghe, L. J. Schaad and J. R. Van Wazer, J. Amer. Chem. Soc., 92, 6107 (1970);

(c) F. Acloque, O. Kahn and A. Dniestrocvski, C. R. Acad. Sci, C. 271 (1970);

(d) R. M. Archibald and P. G. Perkins, Rev. Roum. Chim., 16, 1137 (1971)

(e) F. Choplin and G. Kaufmann, Bull. Soc. Chim. Fr., 387 (1971);

(f) F. Choplin and G. Kaufmann, J. Mol. Structure, 11, 311 (1972).

46. J. C. Bunzli, D. C. Frost and C. A. Mcdowell, J. Electron Spectrosc. Relat. Phenom., 1, 481 (1973).

47. J. L. Berkosky, F. O. Ellison, T. H. Lo and J. W. Rabalais, J. Chem. Phys., 59, 5042 (1973).

48. D. Bettridge, M. Thomson, A. D. Baker and N. R. Kemp., Anal. Chem., 44, 2005 (1972).

49. K. Wittel and S. P. McGlynn, Chem. Reviews, 77, 745 (1977).

50. L. V. Vilkov, P. A. Akishin and G. E. Salova, Z Strukl. Khim., 3, 355 (1965).

51. O. A. Raevsky, J. Mol. Str., 19, 275 (1973).

52. L. E. Sutton, "Tables of Interatomic Distances," spec. publ. No. 11, Chem. Soc. London, 1958; Supplement Spec. Publ. No. 18, (1965).

53. S. Chattopadhyay, Unpublished Results.

54. Emsley and Hall, "The Chemistry of Phosphorus," p. 97, Harper and row, Publishers, London, 1976.

55. P. J. Bassett, D. R. Lloyd, I. H. Hillier and V. R. Saunders, Chem. Phys. Letter., 6, 253 (1970).

56. B. Solouki, P. Rosmus and H. Bock, J. Amer. Chem. Soc., 98, 6054, (1976).

57. S. Cradcock and A. Whiteford, J. Chem. Soc. Faraday, II, 281 (1972).

VITA

Swapan Kumar Chattopadhyay was born in Nabadwip, India on November 7, 1952. He was graduated from P. C. H. C. School, Ranaghat, India in 1967.

He entered Jadavpur University, India in 1967 and graduated from that institution with an M.Sc. degree in Chemistry in 1972.

He entered the Louisiana State University at Baton Rouge in August, 1973. He is presently a candidate for the degree of Doctor of Philosphy in Physical Chemistry.

EXAMINATION AND THESIS REPORT

Candidate: Chattopadhyay, Swapan Kumar

Major Field: Physical Chemistry

Title of Thesis: Ultraviolet Photoelectron Spectroscopic Studies of Dicarboxylic Acids and Phosphorus Compounds.

Approved:

S. P. McGlynn
Major Professor and Chairman

James D. Ingraham
Dean of the Graduate School

EXAMINING COMMITTEE:

James D. Ingraham

Robert V. Hanman

Philip W. West

Kenneth Rader Lea

Date of Examination:

July 13, 1979